Quality Assurance Project Plan

Addendum for the AS/SVE Pilot Test

(Appendix B to Remedial Design Work Plan)

Southeast Rockford Groundwater Site

Area 9/10

Rockford, Illinois

CERCLIS ID No. ILD9801000417

July 3, 2003

Prepared for:

HAMILTON SUNDSTRAND CORPORATION
4747 Harrison Avenue
Rockford, Illinois 61125

Submitted by:

SECOR

SECOR International Incorporated
446 Eisenhower Lane North
Lombard, Illinois 60148

APPENDIX B
QUALITY ASSURANCE PROJECT PLAN ADDENDUM FOR THE AS/SVE PILOT TEST

Remedial Design Work Plan
Area 9/10
Rockford, IL
SECOR Project No.: 13UN.02072.01.0001

July 3, 2003

Prepared for:

HAMILTON SUNDSTRAND CORPORATION
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Rockford, Illinois 61125

Submitted by:

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Prepared in accordance with:
USEPA Guidance for Quality Assurance Project Plans, EPAQA/G-5, December 2002 and,
USEPA Region 5 Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan, Revision 0, June 2000

QUALITY ASSURANCE PROJECT PLAN ADDENDUM
FOR THE
AS/SVE
REMEDIAL DESIGN
SE ROCKFORD AREA 9/10
WINNEBAGO COUNTY, ILLINOIS
(Revision 0)

July 3, 2003

Prepared by: SECOR International Incorporated

Mr. Scott Moyer — Date 7/2/03

Mr. David Curnock — Date 6/30/03

Mr. Brad Barquest — Date 7/2/03

U.S. EPA Region 5 Remedial Project Manager — Date
Mr. Russell Hart

U.S. EPA Region 5 Quality Assurance Reviewer — Date
Ms. Alida Roberman

QUALITY ASSURANCE PROJECT PLAN ADDENDUM
FOR THE
AS/SVE
REMEDIAL DESIGN
SE ROCKFORD AREA 9/10
WINNEBAGO COUNTY, ILLINOIS

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U.S. EPA Region 5 Quality Assurance Reviewer Ms. Alida Roberman	Date

TABLES

FIGURES

ATTACHMENTS

QUALITY ASSURANCE PROJECT PLAN ADDENDUM 1
PILOT TEST

INTRODUCTION

The details regarding the sampling in conjunction with the Pilot Test will be included in this addendum to the Quality Assurance Project Plan (QAPP) for the Southeast Rockford Groundwater Site, Area 9/10, Rockford, Illinois (Site). QAPP elements A3-A5, A8, C1, C2, D1, and D2 can be found in the QAPP submitted on March 31, 2003 and are not included in this document.

A6. PROJECT/TASK DESCRIPTION AND SCHEDULE

The ability for the AS/SVE to effectively treat impacted media will be monitored through sampling and analysis of select in-situ and AS/SVE system parameters. In order to test the effectiveness of the SVE system it will be necessary to obtain data on the following:

- Vapor flow and vacuum induced in the subsurface at the extraction well and at monitoring points;
- Site-specific relationship between vapor flow rate and vacuum induced;
- Effects of SVE on the water table;
- Spatial geometry of vacuum and air flow induced as a result of SVE;
- Site conditions such as preferential pathways, utility conduits, or surface paving that will impact SVE operation;
- Volume of condensate and sediment extracted as a byproduct of the SVE process;
- Contaminant concentrations in extracted vapor; and
- Concentrations of carbon dioxide, oxygen, and methane in extracted vapor.

In order to test the effectiveness of the AS system it will be necessary to obtain data on the following:

- Horizontal and vertical permeability;
- Breakthrough air pressure (injection pressure) required to force air into the saturated soil formation;
- Extent of water table mounding as a result of AS;
- Spatial geometry of air flow induced as a result of AS;
- Site conditions such as preferential air flow pathways or less permeable vadose zone layers that will influence vertical vapor migration;
- Air flow requirements;
- Contaminant concentrations in extracted vapor; and
- Concentrations of carbon dioxide, oxygen, and methane in extracted vapor.

To obtain the necessary data to support these characterizations and evaluations the following activities will be performed:

- SVE Step Tests
- Constant Rate SVE Tests
- AS Tests
- Combined AS/SVE Tests

Planned analytical parameters include:

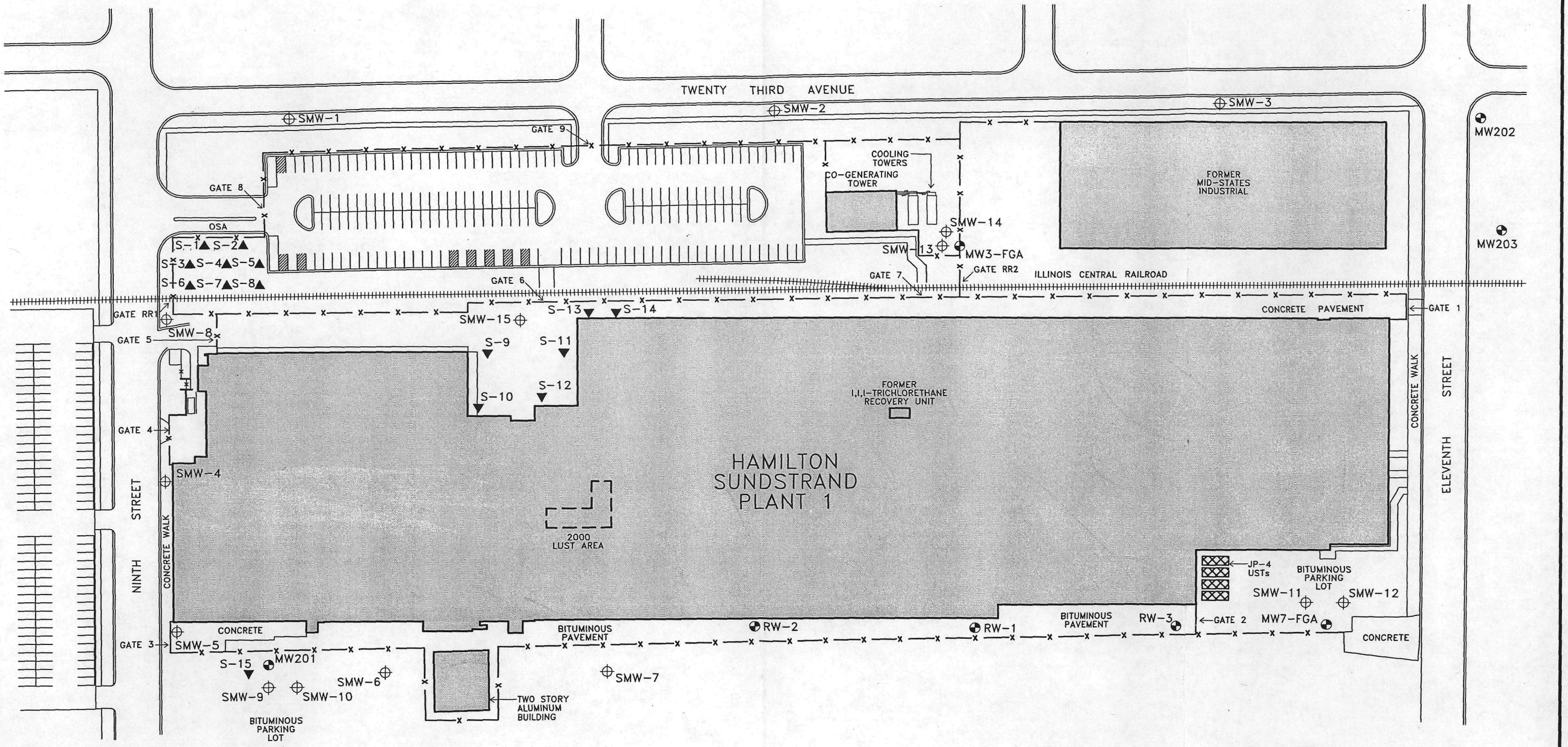
- VOCs (groundwater and soil gas)
    - Using SW-846 Method 8260B for groundwater
    - Using Methods 18/TO-15 for soil gas
- Dissolved oxygen (groundwater), field measurement
- Redox potential (groundwater), field measurement
- pH (groundwater), field measurement
- Carbon dioxide (groundwater), field measurement

Sampling Location Rationale and Numbers of Samples

The sampling locations for soil and groundwater were selected following a review of available information concerning the Site, including description, operational history, decommissioning and closure, and previous investigation activities related to the Hamilton Sundstrand (HS) facility. Table 1 presents the rationale for the selected sample locations and Figure 1 is a map of the Site with Pre-Design Investigation (PDI) sample locations and Figure 2 shows the proposed well configuration for the AS/SVE system with sample locations for the Pilot Test.

Project Schedule

Sampling will be initiated in accordance with the schedule provided in the QAPP submitted on March 31, 2003, following approval of the Work Plan, FSP, QAPP, and Site Health & Safety Plan (HASP) by USEPA in accordance with the Statement of Work (SOW) for RD and the Administrative Order on Consent (AOC).



LEGEND:

- EXISTING MONITORING WELL
- FENCELINE
- PROPOSED SOIL BORING
- PROPOSED SOIL BORING/MONITORING WELL

NORTH

0 20 50 100
SCALE IN FEET

DESIGNED BY:	MGD
DRAWN BY:	GLH
APPROVED BY:	MGD
DATE:	2-12-03

SECOR

PRE-DESIGN INVESTIGATION SAMPLING LOCATIONS

HAMILTON SUNDSTRAND
AREA 9/10
ROCKFORD, ILLINOIS

JOB NO. 13UN.02072.00 FIGURE 1

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GUARD STATION

GATE 8

PARKING

NINTH STREET

(EXISTING) VESM-1
(EXISTING) VESM-2
(EXISTING) VE-1
AS-1
(EXISTING) VESM-3
ASDM-3
VM-3I
VM-3D
VE-2
ASDM-1
ASDM-2
ASDM-4

GROUND WATER FLOW

(EXISTING) VEDM-4

VM-4D
VM-4I
VM-4S

(EXISTING) VEDM-6

(EXISTING) VEDM-5

VM-5S VM-5I VM-5D

ILLINOIS CENTRAL RAILROAD

GATE RR1

LEGEND:

- △ SOIL VAPOR EXTRACTION WELL
- ▲ VADOSE ZONE MONITORING WELL
- ◒ AIR SPARGING WELL
- ⊗ AIR SPARGE MONITORING WELL

NOTE: CONCEPTUAL PURPOSES ONLY. LAYOUT FEATURES ARE BASED ON DRAWINGS PREPARED BY HARDING LAWSON ASSOCIATES, INC. 1992.

NORTH

0 2 5 10
SCALE IN FEET

DESIGNED BY:	LW
DRAWN BY:	GH
APPROVED BY:	
DATE:	6-12-03

SECOR

PILOT TEST SITE PLAN

HAMILTON SUNDSTRAND
AREA 9/10
ROCKFORD, ILLINOIS

JOB NO. 13UN.02072.00 FIGURE 2

S:\PROJECTS\013 lombard projects\13UN.02072.00 Rockford\secor rd\pilot test work plan\qapp\061 figure 2.dwg gh 6-12-03

TABLE 1
Rationale for Well Placements Associated with the Pilot Test
Remedial Design
Area 9/10
Rockford, Illinois

Well Number	Boring depth/ Screen Interval Below Ground Surface	Location	Purpose
ASDM 1 through 4	Screen interval approximately 25-40 feet	OSA	To enable collection of groundwater and sparged gas samples from both the vadose and saturated zone and depth to water table measurements during the Pilot Test. Groundwater samples for VOCs will also be collected.
VESM 1 through VESM 3 (Existing); VM-4S, VM-5S	Screen interval approximately 2.5-4.5 feet	OSA	To collect soil gas analytical, induced air flow and induced vacuum data from the upper part of the vadose zone to aid in the RD Pilot Test.
VM-3I through VM-5I	Screen interval approximately 15 - 17 feet	OSA	To collect soil gas analytical, induced air flow and induced vacuum data from the intermediate part of the vadose zone to aid in the RD Pilot Test.
VM-3D through VM-5D	Screen interval approximately 24-26 feet	OSA	To collect soil gas analytical, induced air flow and induced vacuum data from the deeper part of the vadose zone to aid in the RD Pilot Test
VEDM 4 through VEDM 6 (Existing)	Screen interval approximately 9-19 feet	OSA	To collect soil gas analytical information to aid in the design of the RD.
VE-1 (Existing)	Screen interval approximately 9-19 feet	OSA	To extract soil gas during the operation and evaluation of the RD Pilot Test.
VE-2	Screen interval approximately 22-27 feet	OSA	To extract soil gas during the operation and evaluation of the RD Pilot Test.
AS-1	Screen interval approximately 38-40 feet	OSA	To inject air beneath the water table during the operation and evaluation of the RD Pilot Test.
SMW-8	Screen interval approximately 25-40 feet	West side of the HS property, along the east side of 9th Street.	To collect groundwater monitoring data from the upper interval of the saturated zone in that area of the site during the Pilot Test evaluation.

A7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The purpose of this section is to document the Data Quality Objectives (DQO) process of the project and to establish performance criteria for the mandatory systematic planning process and measurement system that will be employed in generating the data.

Data Quality Objectives

Per the Region V QAPP Instructions Manual (Revision 0, June 2000), the DQO process is a strategic planning approach that is designed to ensure that the type, quantity, and quality of environmental data used in decision-making are appropriate for the intended application. The systematic procedure for defining the DQO criteria involve addressing the following:

State the Problem

The Record of Decision (ROD) states that source materials (volatile organic compounds) exist within Area 9/10 that require remedial attention.

Identify the Decision

The decision is how to address the source materials through the application of two remedial technologies: 1) soil vapor extraction and 2) enhanced air sparging. The goal of the RD is to prepare a remedial design package utilizing the selected remedial technologies.

Identify Inputs to the Decision

The PDI in Area 9/10 within the vicinity of the HS Facility will be used to gather data which can be used to facilitate the design of the chosen remedial technologies. Soil gas and groundwater samples will be collected from the AS/SVE test area during the Pilot Study in order to assess the effectiveness of the system.

Define the Study Boundaries

The boundaries of the RD are defined as Area 9/10 of the SER Site with emphasis on the vicinity of the HS facility. The boundaries of the Pilot Test are confined to the OSA portion of the HS facility.

Develop a Decision Rule

The results of the soil vapor and groundwater samples collected from the AS/SVE system during the Pilot Test will be used to help evaluate the system performance. Of particular interest will be the radii of influence and the ability of the system to remove contaminant mass.

Specify Limits on Decision Errors

The soil boring/monitoring points location rationale is described in Table 1 and is based upon the need for vertical and horizontal delineation of the OSA for the AS/SVE Pilot Test design, and to place wells and monitoring points for the AS/SVE system. A Field Sampling Plan (FSP) will be available during AS/SVE field activities. The FSP will outline the methodology to be used for sampling and sample handling. Adherence to the FSP should reduce the amount of Decision Errors made in the field. Approved USEPA test methods will be used for the analysis of soil and groundwater samples. Some parameters will be measured and recorded in the field.

Sample matrices, analytical parameters, frequencies of sample collection, and analytical levels to be used during investigation activities are presented in Table 2.

TABLE 2
Sample Matrix, Frequency, and Analytical Levels for the Pilot Test
Remedial Design
Area 9/10
Rockford, Illinois

Medium	Method	Data Package Level	Sample No.	Dup. Sample	Field (Rinse) Blanks	Trip Blanks	Matrix Spikes	Notes
Groundwater (VOCs)	SW846 Method 8260B	2	22	2	(c)	(a)	5%	(b)
Soil gas (VOCs)	USEPA Methods 18/TO-15	2	44					(b)
Soil Gas Methane, CO_2, O_2	Field Measurement		34					
Groundwater (Redox)	Field Measurement		34			--		(b)
Groundwater (dissolved oxygen)	Field Measurement		34					(b)
Groundwater (dissolved CO_2)	Field Measurement		34					(b)
Groundwater (pH)	Field Measurement		34					
Soil Gas (Helium)	Field Measurement		60					

Notes:
(a) One trip blank will be included in each sample cooler submitted to the laboratory for VOC analysis only.
(b) *Duplicates will be selected based on field conditions and observations.*
(c) One rinse blank per representative activity will be collected for groundwater VOCs.

A8. SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

All aspects of the project will be completed by environmental professionals trained to complete their required duties. Samplers will be trained in SECOR standard operating procedures (SOPs) and specific understanding of this project SOW and QA data needs.

The Field Manager, Technical Team, and drilling crew will have all had 40-hour OSHA HAZWOPER training (40 CFR 1910.120) and/or the 8 Hour refresher training within 12 months of the field activities. The Pilot Test startup, evaluation and monitoring will be performed under the supervision of a professional engineer licensed in the State of Illinois.

A9. DOCUMENTATION AND RECORDS

QA Project Plan

QAPP versions, updates, distribution and disposition will be the responsibility of the PC and PM. If necessary, new versions or updates of the QAPP will be forwarded to the individuals on the distribution list and the subcontracted laboratories by the Project Coordinator.

Sample Designation

Samples will be designated according to the following procedures. The equipment used to collect samples will be noted, along with the time of sampling, sample description, depth at which the sample was collected, volume and number of containers. Sample site-specific identification number will be assigned prior to sample collection. The site-specific sample number should consist of the following:

- Project Identification Code: A designation will be used to identify the site where the sample was collected. The project identification code for Pilot Test activities is PT.

- Sample Matrix and Location Code: Each sample should be identified in the field notebook by an alpha/numeric code corresponding to the sample matrix/type, followed by a three-digit sample location number. The alpha-numeric codes which will be used for the PT are:

  - FB - Field blank
  - GW - Groundwater samples
  - SB - Soil boring samples
  - TB - Trip blank
  - FD - Field duplicate

  The location code will follow the sample type code. The location code consists of a two- to five-digit numeric or alpha/numeric code that indicates the sample location. Location codes lower than 10 will be preceded by '0', e.g. '01'; '02'; etc. Private well samples location codes will be letters. Soil, field duplicate, trip blank, and field duplicate samples will use a consecutive numbering system starting at 01.

  The Round Code will follow the location code. The round numbers for all samples will be a two-digit number preceded by a hyphen, beginning with 01. Round 01 represents samples collected during the PT.

- Examples of Sample numbers:

  - PT-SGVE01-01= PT, soil vapor sample from vapor extraction well VE01, round 1
  - PT-GWMW22-01 = PT, groundwater sample from well MW22, round 1
  - PT-GWFD01-01 = PT, duplicate groundwater sample number 01
  - PT-GWFB01-01 = PT, field blank 1, round 1

The sample packaging and shipment procedures summarized below will ensure that the samples will arrive at the laboratory with the chain-of-custody intact. Examples of field custody documents are found in Attachment C.

Field Operation Records

Field Logs

Field logbooks will provide the means of recording data collection activities performed. Field logbooks, field survey books, and/or notebooks will be bound. Logbooks will be assigned to field personnel and will be the responsibility of the individual person until field activities are concluded, at which time the field notebook will be returned to the project file or project manager. Each logbook will be identified by the project-specific document number. The title page of each logbook will contain the following:

- Person to whom the logbook is assigned
- Logbook number
- Project name
- Project start date
- Project end date (at the end of field activities)
- SECOR project number

Entries into the logbook will contain a variety of information. At the beginning of each day's activities, the date, start time, weather, names of personnel onsite, level of personal protection being used, and equipment and/or subcontractors onsite will be noted. Each page of the field notebook will be initialed and dated by the author. The names of visitors to the Site, field sampling or investigation team personnel and the purpose of their visit will also be recorded in the crew chief field notebook. Unusual conditions will be recorded.

Measurements made and field and QC samples collected will be recorded. All entries will be made in ink and no erasures will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark. Whenever a sample is collected, or a measurement made, a detailed description of the location of the station, which includes direction and distance measurements, shall be recorded. The number of photographs taken of the station, if any, will also be noted. All equipment used to make measurements will be identified, along with the date of calibration.

The equipment used to collect samples will be noted, along with the time of sampling, sample description, and depth at which the sample was collected. Sample identification numbers will be noted for both field and QC samples.

Sample Labeling

Samples will be labeled and covered with transparent tape after marking, and will include the following information:

- Laboratory
- Sample identification number
- Project number
- Date and time of collection
- Sample matrix (soil or water)
- Collection mode (discrete or composite)
- Analysis requested

- Name of sampler(s)
- Type of preservative (if applicable)

Sample Custody, Storage and Shipping Documentation

All samples will be accompanied by a properly completed Chain-of-Custody (COC) form. The sample numbers and locations will be listed on the COC form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to an off-site laboratory, or to/from a secure storage area.

Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed COC record enclosed in each sample box or cooler. Shipping containers will be secured with strapping tape for shipment to the laboratory. The preferred procedure includes use of a custody seal attached to the front right and back left of the cooler. The cooler will be strapped shut with strapping tape in at least two locations.

All shipments will be accompanied by the COC record identifying the contents. The original record will accompany the shipment, and remaining copies will be retained by the sampler and returned to the Project Manager or project file. If the samples are sent by common carrier, a bill of lading shall be used. Receipts of bills of lading will be retained as part of the permanent documentation. Commercial carriers will not be required to sign off on the custody forms as long as the custody forms are sealed inside the sample cooler and the custody seals remain intact.

Sample Location Documentation

All boring/monitoring points locations will be surveyed with respect to a known geodetic datum providing measuring point elevations (relative to mean sea level) and coordinates (relative to Illinois State Plane Coordinates) by a surveyor licensed in the State of

Illinois. Previously existing monitoring points may also be re-surveyed to help assure accurate baseline elevation data. Sample ports for the SVE system will be displayed on the SVE schematic.

Data Report Packages

Data report packages from the laboratory will be Standard Data Deliverable Package (Data Package Level 2) including:

- Cover Page – signed by the laboratory project manager
- Case Narrative – only if technical problems occurred or requested by the client
- Sample Information
- Results
- Laboratory Chronicle (LabChron)
- Quality Control (Default QC Types – Preparation Batch QC Reported)
- Quality Assurance Methods References and Notes
- Chain-of-Custody

GROUP B
DATA GENERATION AND ACQUISITION

B1. SAMPLING PROCESS DESIGN

The Pilot Test has been designed to facilitate the collection of sufficient data to test the effectiveness of the AS/SVE system as a remedy as defined in the ROD. To obtain the necessary data to following activities will be performed:

- Soil vapor sampling will be conducted from the soil vapor extraction well VE-1 or VE-2 during AS/SVE testing. The 14 vadose zone monitoring points will be used to monitor variations in pressure and provide soil gas samples during the AS and AS/SVE portions of the Pilot Tests.

- Groundwater monitoring points (ASDM 1 through 4) will be installed to investigate the upper part of the saturated zone. Monitoring well SMW-8 will also be utilized for groundwater monitoring. The new monitoring points, along with other existing monitoring wells associated with the Site, will be sampled to collect baseline and operational data to support of the Pilot Test.

B2. SAMPLING METHODS REQUIREMENTS

The following subsection discusses the procedures involved in collecting samples during the Pilot Test.

Procedures for Collecting Samples

Soil vapor samples will be collected from sampling ports in the system. Procedures for collecting soil vapor samples for VOC analysis are included in USEPA Method 18 which Is presented in Attachment F. Samples for VOC analysis will be collected in Tedlar

bags, which will be sent to the laboratory. The laboratory will transfer the sample from the Tedlar bag to a Summa® canister within 72 hours of time of sample collection, increasing the sample hold time to 28 days.

Groundwater samples will be collected after purging the monitoring well. Procedures for the completion of monitoring wells, and for monitoring well development are included in the QAPP submitted on March 31, 2003. The extent and distribution of groundwater contamination will be characterized through the analyses of VOCs. Samples for VOC analysis will be collected in 40-ml glass vials provided by the laboratory conducting the analysis. Disposable nitrile gloves will be worn during the sampling event. Samples will be collected using bailers or down hole submersible pumps with dedicated polyethylene tubing. If a submersible pump is utilized, a flow cell may be used for field measurement of pH, temperature, conductivity, dissolved oxygen, dissolved carbon dioxide, and ORP. VOC samples will be collected by slowly pumping or decanting the water into 40 ml glass vials. Vials will be filled until a convex meniscus is present and then capped. The cap will then be secured and checked for trapped air. Any VOC samples with entrained air will be discarded, and new samples collected. Duplicate and field blank samples will also be collected in accordance with Table 2.

Sampling methods, equipment and decontamination are further described in the FSP. Operating instructions for equipment used in collection field measurements are included in Attachment E. Sample volumes preservatives and holding times are given in Table 3. Additional information regarding the sampling methodology are included in SOPs A-18, A-19, and A21, which are presented in the QAPP submitted on March 31, 2003. It will be the responsibility of the Field Site Manager and the Technical Team to determine if there is a sampling error in the field and how to take corrective action.

B3. SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Immediately after samples are collected the proper sample information will be written on the sample labels and the samples will be placed in a cooler. Groundwater samples will be placed in a cooler with ice. Before shipping, Chain-of-Custody forms will be filled out for the samples, signed, and the proper copies will be placed in the coolers with the samples. After insuring that enough ice is in the coolers to keep the samples at 4 (+/-2) degrees Celsius, then the coolers can be sealed and shipped to the laboratory for overnight delivery. Examples of sample labels and custody forms are in Attachment C. Procedures for water, soil, and waste handling are included in SOPs A-22 and A-24.

B4. ANALYTICAL METHODS REQUIREMENTS

Soil vapor and groundwater samples collected during AS/SVE Pilot Test activities at the Site will be analyzed by Severn Trent Laboratories (STL). The soil vapor and groundwater samples will be analyzed for VOCs by the methods outlined in Table 3. A copy of Method 8260B (groundwater analysis) and Method TO-15 (soil vapor analysis) are provided in Attachment F. Samples will be analyzed at standard turn-around times of 21 days.

Reporting Limits

Reporting limits for each of the analytical methods that will be met by STL are detailed in Attachment A of this document. If samples are diluted, the matrix reporting limits will be calculated as the detection multiplied by the dilution factor.

Holding Times

Sample holding time, sample containers, and preservatives (if required) are detailed on Table 3. Samples will be analyzed with their required holding times.

TABLE 3
Sample Containers, Preservatives, and Holding Times
Pilot Test
Remedial Design
Area 9/10
Rockford, Illinois

Matrix	Parameter/ Analytical Method	Sample Container	Preservative	Holding Time To Extraction
Groundwater	VOCs (5030B/8260B)	40 ml glass vials	HCl; pH <2 Cool 4 +/- 2°C	14 Days
Soil Gas	VOCs (method 18/TO-15)	Tedlar bags (1 liter)	Cool 4+/- 2° C	72 hours;28 days*

- If samples show evidence of effervescence (i.e., bulging septa, fizzing, hissing when auto-sampler punctures septa, etc.) upon sample receipt, the laboratory will notify SECOR

* Soil gas samples must be shipped to the laboratory each day for overnight delivery. Upon receipt, the laboratory will transfer the samples to Summa® canisters, increasing the hold time to 28 days.

B5. QUALITY CONTROL REQUIREMENTS

Field QC samples are submitted as separate samples to the laboratory and reported accordingly on the data reports. Specific requirements are outlined below. Field blanks, rinsate blanks, matrix spikes, matrix spike duplicates, and field duplicates are used during this program.

Blanks

Field Blanks

Field blanks consist of deionized water that is taken to the field, transferred to the appropriate container (one liter amber glass bottle), preserved, and otherwise treated as a sample during the course of the sampling event. Field blanks will be collected at a rate of one per 20 samples analyzed.

Spikes

Matrix Spikes

A matrix spike is an aliquot of sample spiked with a known concentration of the analyte of interest. Percent recovery of the known concentration of added analyte is used to assess accuracy of the analytical process. The spiking occurs prior to the sample preparation and analysis. The matrix spike is used to document the accuracy of a method due to sample matrix and not to control the analytical process. The analysis of matrix spikes is a measure of accuracy and is calculated by percent recovery. Matrix spikes for water will be collected in the field and analyzed at a rate of one per 20 samples analyzed.

Matrix Spike Duplicate

Matrix spike duplicates are prepared in the same manner as the matrix spike samples and are uses to assess the precision of the matrix spike analysis. Matrix spike duplicates for water will be collected in the field and analyzed at a rate of one per 20 samples analyzed.

Field Duplicates

Field duplicates consist of soil vapor or groundwater samples collected in the field using a consistent methodology as the investigation sample (i.e, locations selected for field duplicates are sampled twice rather than once). Field duplicate samples are transferred to an appropriate laboratory-supplied sample container and treated as an independent sample with the exception that field duplicate samples are labeled in such a manner as to not indicate the time or place in which they were collected.

B6. INSTRUMENT /EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

Laboratory Instrumentation

As part of STL's QA Program Plan, a routine preventative maintenance program is conducted to minimize the occurrence of instrument failure and other system malfunctions. The analysts regularly perform routine instrument maintenance tasks (or coordinate with the vendor). All maintenance that is performed is in accordance with the manufacturer's specifications and is documented in the laboratory's pre-formatted and bound maintenance logbooks.

Each analytical instrument is assigned an instrument maintenance logbook. All maintenance activities are recorded in the maintenance log. The information entered in the maintenance log includes:

- Date of service or maintenance.
- Person performing service or maintenance.
- Type of service performed and reason for service.
- Replacement parts installed (if appropriate).
- Miscellaneous information.

If service is performed by the manufacturer, a copy of the service record (when available) is affixed to the notebook page, or cross-referenced in the notebook to a separate maintenance file. The service record should include sufficient detail to describe the service performed (e.g., not just "service call," but "replaced pump motor gear"). If the service record does not define this information, it must be written separately into the maintenance log.

Preventative maintenance and repairs that cannot be performed by laboratory staff are contracted to the manufacturer's service section or to an authorized maintenance vendor. Laboratory service agreements provide for preventive maintenance, emergency service,

and emergency shipping of spare parts. Annual service of the laboratory balances is an example of contracted preventive maintenance.

Examples of maintenance procedures and suggested frequencies for major analytical instrumentation are summarized in Table 4. Instrument specific information is provided in the respective instrument manuals and in the laboratory SOPs (Attachment B).

TABLE 4
Example: Laboratory Equipment and Maintenance
Remedial Design
Area 9/10
Rockford, Illinois

Instrument	Procedure	Frequency
Hewlett Packard GC/MS	Check for correct column flow and/or inlet pressure	Daily
	Check inlets, and baseline level.	Daily
	Check relative abundance and mass assignments	Daily
	Check liquid nitrogen and carrier gas levels.	Daily
	Replace Electron mulitplier	As required
	Clean ion source	As required
	Replace trap	As required
	Change pump oil	Semi-annually
	Replace exhaust filters on mechanical pump	Annually

B7. INSTRUMENT CALIBRATION AND FREQUENCY

Laboratory Instrument Calibration

Calibration procedures for a specific laboratory instrument will consist of initial calibrations (3 or 5-points), initial calibration verifications, and continuing calibration verification. For a description of the calibration procedures for a specific laboratory instrument, refer to the applicable SOPs in Attachment B of this QAPP. The SOP for each analysis performed in the laboratory describes the calibration procedures, their frequency, acceptance criteria,

and the conditions that will require recalibration. Initial calibration will be verified using an independently prepared calibration verification standard.

The laboratory maintains an analysis logbook (hardcopy or electronic) for each instrument which contains the following information: instrument identification, date of calibration, analyst, calibration solutions run and the samples associated with these calibrations.

Table 5 provides a summary of the laboratory's calibration procedures for the requested analyses.

TABLE 5
Example of Calibration and Corrective Action Procedures
Remedial Design
Area 9/10
Rockford, Illinois

Analysis	EPA Method	Calibration Technique	Frequency	Acceptance Criteria	Corrective Action
Volatiles	TO15	Calibration Curve (5 Point minimum)	Initially; thereafter as the continuing calibration fails	%RSD≤30% with up to two analytes <40%	1) Evaluate System 2) Recalibrate as necessary
		BFB Tune	Prior to the ICAL and prior to every 24 hour continuing calibration	Must meet mass vs. ion abundance criteria as listed in the method.	1) Evaluate System. 2) Re-tune the instrument.
		Continuing Calibration	Every 24 hours	%D≤30% with up to 4 analytes %D≤40%	1) EvaluateSystem 3) 2) Repeat Calibration check Recalibrate as necessary (new ICAL)Reanalyze affected samples
		Method Blank	Every 20 samples or following CC	< RL	1) Rerun 2) Evaluate Batch (CAR/Narrate) 3) Reanalyze as necessary
		LCS	Every 20 samples	All non-polar analytes within 70-130% Recovery with up to two within 60-140% Recovery. All polar analytes 60-140% Recovery with up to two polar analytes within 45-155% Recovery.	1) Rerun 2) Evaluate batch (CAR/Narrate) 3) Reanalyze as necessary
		Duplicate	Every 20 samples	<25% RPD for target analytes >5x RL. (no criteria for methanol and n-butanol)	1) Rerun 2) Evaluate batch
		Surrogate	Every sample	70-130% Recovery	1) Rerun 2) Reanalyze as necessary (CAR/Narrate)

TABLE 5
Example of Calibration and Corrective Action Procedures
Remedial Design
Area 9/10
Rockford, Illinois

Analysis	EPA Method	Calibration Technique	Frequency	Acceptance Criteria	Corrective Action
		Internal Standard Area	Every Sample	+/-40% Recovery of internal standard Area compared with Continuing Calibration.	1) If result of instrument malfunction, correct problem and reanalyze samples. 2) If matrix related, reanalyze to confirm.
		RT's for Internal Standards	Each initial and continuing calibration	± 20 seconds	1) If result of instrument malfunction, correct problem and reanalyze samples. 2) If matrix related, reanalyze to confirm.

Note: Matrix Spikes: Acceptance Criteria is not applicable if the sample concentration exceeds the spike level by 4 times.

ATTACHMENT A
QAPP ADDENDUM FOR THE AS/SVE PILOT TEST
LABORATORY MDLS, RLS, AND CONTROL LIMITS

SECOR Project NO.: 13UN.02072.01.0001

July 3, 2003

STL Knoxville TO-15 Limits

#	Compound	RL	Units	MDL	Units	T	A	AMT	Units	LCL	UCL	RPD	T	A	AMT	Units	LCL	UCL	RPD
196	Benzene	0.2	ppb(v/v)	0.06	ppb(v/v)	C	Y	10	ppb(v/v)	70	130	25	C	Y	10	ppb(v/v)	70	130	25
220	Benzyl chloride	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
343	Bromomethane	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
463	Carbon tetrachloride	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
521	Chlorobenzene	0.2	ppb(v/v)	0.06	ppb(v/v)	C	Y	10	ppb(v/v)	70	130	25	C	Y	10	ppb(v/v)	70	130	25
550	Chloroethane	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
569	Chloroform	0.2	ppb(v/v)	0.04	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
574	Chloromethane	0.5	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
3261	1,2-Dibromoethane (EDB)	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
904	1,2-Dichlorobenzene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
907	1,3-Dichlorobenzene	0.2	ppb(v/v)	0.04	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
910	1,4-Dichlorobenzene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
924	Dichlorodifluoromethane	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
933	1,1-Dichloroethane	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
936	1,2-Dichloroethane	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
948	cis-1,2-Dichloroethene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
943	1,1-Dichloroethene	0.2	ppb(v/v)	0.04	ppb(v/v)	C	Y	10	ppb(v/v)	70	130	25	C	Y	10	ppb(v/v)	70	130	25
986	1,2-Dichloropropane	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
998	cis-1,3-Dichloropropene	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
1000	trans-1,3-Dichloropropene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
1015	1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
1332	Ethylbenzene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
1489	Hexachlorobutadiene	0.2	ppb(v/v)	0.03	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
1811	Methylene chloride	0.5	ppb(v/v)	0.24	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2355	Styrene	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2439	1,1,2,2-Tetrachloroethane	0.2	ppb(v/v)	0.04	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2445	Tetrachloroethene	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2489	Toluene	0.2	ppb(v/v)	0.09	ppb(v/v)	C	Y	10	ppb(v/v)	70	130	25	C	Y	10	ppb(v/v)	70	130	25
2515	1,2,4-Trichlorobenzene	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2518	1,1,1-Trichloroethane	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2522	1,1,2-Trichloroethane	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2525	Trichloroethene	0.2	ppb(v/v)	0.06	ppb(v/v)	C	Y	10	ppb(v/v)	70	130	25	C	Y	10	ppb(v/v)	70	130	25
1428	Trichlorofluoromethane	0.2	ppb(v/v)	0.04	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2566	1,1,2-Trichloro-1,2,2-trifluoroethane	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2587	1,2,4-Trimethylbenzene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2592	1,3,5-Trimethylbenzene	0.2	ppb(v/v)	0.06	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2613	Vinyl chloride	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2940	m-Xylene & p-Xylene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
2623	o-Xylene	0.2	ppb(v/v)	0.05	ppb(v/v)		Y	10	ppb(v/v)	70	130	25		Y	10	ppb(v/v)	70	130	25
337	4-Bromofluorobenzene					X	Y	4	ppb(v/v)	70	130	0	X	Y	4	ppb(v/v)	70	130	0
2735	1,2-Dichloroethane-d4					X	Y	8	ppb(v/v)	70	130	0	X	Y	8	ppb(v/v)	70	130	0
2740	Toluene-d8					X	Y	8	ppb(v/v)	70	130	0	X	Y	8	ppb(v/v)	70	130	0

STL Chicago
Method Limit Report

Project: Secor - Remedial Design SE Rockford Area 9/10
Date: 3/17/03

Method Description	Analytical Method	Test Matrix	Units	MDL	Lab RL	LCL	UCL	RPD	SLL	SUL
Method: Leachable, Metals Analysis (ICAP) (6010L)										
Arsenic	6010B	TCLP	mg/L	0.01	0.1	80	120	20		
Barium	6010B	TCLP	mg/L	0.01	1	80	120	20		
Cadmium	6010B	TCLP	mg/L	0.002	0.05	80	120	20		
Chromium	6010B	TCLP	mg/L	0.01	0.05	80	120	20		
Lead	6010B	TCLP	mg/L	0.005	0.05	80	120	20		
Selenium	6010B	TCLP	mg/L	0.01	0.1	80	120	20		
Silver	6010B	TCLP	mg/L	0.005	0.05	80	120	20		
Method: Mercury (CVAA) (7470)										
Mercury	7470A	TCLP	ug/L		2	80	120	20		
Method: Volatile Organics (8260B)										
1,1,1,2-Tetrachloroethane	8260B	Water	ug/L	0.21	1	70	134	20		
1,1,1-Trichloroethane	8260B	Water	ug/L	0.22	1	66	129	20		
1,1,2,2-Tetrachloroethane	8260B	Water	ug/L	0.25	1	72	127	20		
1,1,2-Trichloroethane	8260B	Water	ug/L	0.33	1	69	138	20		
1,1-Dichloroethane	8260B	Water	ug/L	0.2	1	69	127	20		
1,1-Dichloroethene	8260B	Water	ug/L	0.19	1	54	127	20		
1,1-Dichloropropene	8260B	Water	ug/L	0.24	1	70	128	20		
1,2,3-Trichlorobenzene	8260B	Water	ug/L	0.24	1	75	123	20		
1,2,3-Trichloropropane	8260B	Water	ug/L	0.2	1	71	126	20		
1,2,4-Trichlorobenzene	8260B	Water	ug/L	0.23	1	77	123	20		
1,2,4-Trimethylbenzene	8260B	Water	ug/L	0.2	1	72	126	20		
1,2-Dibromo-3-chloropropane	8260B	Water	ug/L	0.46	1	66	123	20		
1,2-Dibromoethane (EDB)	8260B	Water	ug/L	0.25	1	71	135	20		
1,2-Dichlorobenzene	8260B	Water	ug/L	0.24	1	74	119	20		
1,2-Dichloroethane	8260B	Water	ug/L	0.25	1	63	133	20		
1,2-Dichloroethene (total)	8260B	Water	ug/L	0.42	1	72	121	20		
1,2-Dichloropropane	8260B	Water	ug/L	0.22	1	71	132	20		
1,3,5-Trimethylbenzene	8260B	Water	ug/L	0.2	1	69	123	20		
1,3-Dichlorobenzene	8260B	Water	ug/L	0.23	1	73	121	20		
1,3-Dichloropropane	8260B	Water	ug/L	0.23	1	71	133	20		
1,4-Dichlorobenzene	8260B	Water	ug/L	0.22	1	74	121	20		
2,2-Dichloropropane	8260B	Water	ug/L	0.2	1	56	141	20		
2-Butanone (MEK)	8260B	Water	ug/L	1.7	5	54	145	20		
2-Chlorotoluene	8260B	Water	ug/L	0.22	1	69	120	20		
2-Hexanone	8260B	Water	ug/L	1.2	5	70	144	20		
4-Chlorotoluene	8260B	Water	ug/L	0.22	1	68	120	20		

Method Description	Analytical Method	Test Matrix	Units	MDL	Lab RL	LCL	UCL	RPD	SLL	SUL
4-Methyl-2-pentanone (MIBK)	8260B	Water	ug/L	0.92	5	66	147	20		
Acetone	8260B	Water	ug/L	1.5	5	43	150	20		
Benzene	8260B	Water	ug/L	0.2	1	74	116	20		
Bromobenzene	8260B	Water	ug/L	0.22	1	77	121	20		
Bromochloromethane	8260B	Water	ug/L	0.19	1	57	133	20		
Bromodichloromethane	8260B	Water	ug/L	0.23	1	76	129	20		
Bromoform	8260B	Water	ug/L	0.22	1	73	139	20		
Bromomethane	8260B	Water	ug/L	0.18	1	51	152	20		
Carbon disulfide	8260B	Water	ug/L	0.4	5	29	136	20		
Carbon tetrachloride	8260B	Water	ug/L	0.24	1	66	136	20		
Chlorobenzene	8260B	Water	ug/L	0.22	1	76	124	20		
Chloroethane	8260B	Water	ug/L	0.21	1	68	135	20		
Chloroform	8260B	Water	ug/L	0.23	1	74	128	20		
Chloromethane	8260B	Water	ug/L	0.16	1	56	129	20		
cis-1,2-Dichloroethene	8260B	Water	ug/L	0.21	1	78	126	20		
cis-1,3-Dichloropropene	8260B	Water	ug/L	0.22	1	75	123	20		
Dibromochloromethane	8260B	Water	ug/L	0.23	1	74	137	20		
Dibromomethane	8260B	Water	ug/L	0.26	1	66	131	20		
Dichlorodifluoromethane	8260B	Water	ug/L	0.14	1	56	136	20		
Ethylbenzene	8260B	Water	ug/L	0.2	1	74	121	20		
Hexachlorobutadiene	8260B	Water	ug/L	0.24	1	56	147	20		
Isopropylbenzene	8260B	Water	ug/L	0.21	1	67	123	20		
m&p-Xylenes	8260B	Water	ug/L	0.39	2	71	125	20		
Methylene chloride	8260B	Water	ug/L	0.19	1	52	133	20		
Methyl-tert-butyl-ether (MTBE)	8260B	Water	ug/L	0.21	1	52	156	20		
Naphthalene	8260B	Water	ug/L	0.34	1	69	125	20		
n-Butylbenzene	8260B	Water	ug/L	0.22	1	71	118	20		
n-Propylbenzene	8260B	Water	ug/L	0.25	1	67	123	20		
o-Xylene	8260B	Water	ug/L	0.21	1	72	124	20		
p-Isopropyltoluene	8260B	Water	ug/L	0.22	1	67	126	20		
sec-Butylbenzene	8260B	Water	ug/L	0.22	1	69	124	20		
Styrene	8260B	Water	ug/L	0.23	1	80	125	20		
tert-Butylbenzene	8260B	Water	ug/L	0.21	1	69	123	20		
Tetrachloroethene	8260B	Water	ug/L	0.2	1	69	128	20		
Toluene	8260B	Water	ug/L	0.21	1	71	122	20		
trans-1,2-Dichloroethene	8260B	Water	ug/L	0.21	1	64	119	20		
trans-1,3-Dichloropropene	8260B	Water	ug/L	0.24	1	76	126	20		

Method Description	Analytical Method	Test Matrix	Units	MDL	Lab RL	LCL	UCL	RPD	SLL	SUL
Trichloroethene	8260B	Water	ug/L	0.21	1	70	120	20		
Trichlorofluoromethane	8260B	Water	ug/L	0.22	1	62	141	20		
Vinyl chloride	8260B	Water	ug/L	0.18	1	67	137	20		
Surrogate										
1,2-Dichloroethane-d4 (surr)	8260B	Water	ug/L						61	131
4-Bromofluorobenzene (surr)	8260B	Water	ug/L						73	122
Dibromofluoromethane (surr)	8260B	Water	ug/L						66	132
Toluene-d8 (surr)	8260B	Water	ug/L						78	128
Method: Volatile Organics (8260B)										
1,1,1,2-Tetrachloroethane	8260B	Solid	ug/Kg	0.73	5	83	123	20		
1,1,1-Trichloroethane	8260B	Solid	ug/Kg	0.61	5	63	133	20		
1,1,2,2-Tetrachloroethane	8260B	Solid	ug/Kg	0.64	5	68	139	20		
1,1,2-Trichloroethane	8260B	Solid	ug/Kg	0.71	5	71	143	20		
1,1-Dichloroethane	8260B	Solid	ug/Kg	0.88	5	63	133	20		
1,1-Dichloroethene	8260B	Solid	ug/Kg	1	5	51	132	20		
1,1-Dichloropropene	8260B	Solid	ug/Kg	0.8	5	78	148	20		
1,2,3-Trichlorobenzene	8260B	Solid	ug/Kg	0.99	5	75	125	20		
1,2,3-Trichloropropane	8260B	Solid	ug/Kg	1.1	5	71	129	20		
1,2,4-Trichlorobenzene	8260B	Solid	ug/Kg	0.79	5	76	127	20		
1,2,4-Trimethylbenzene	8260B	Solid	ug/Kg	0.82	5	74	133	20		
1,2-Dibromo-3-chloropropane	8260B	Solid	ug/Kg	1.1	5	59	124	20		
1,2-Dibromoethane (EDB)	8260B	Solid	ug/Kg	0.76	5	72	133	20		
1,2-Dichlorobenzene	8260B	Solid	ug/Kg	0.73	5	85	120	20		
1,2-Dichloroethane	8260B	Solid	ug/Kg	0.58	5	69	125	20		
1,2-Dichloroethene (total)	8260B	Solid	ug/Kg	1.9	5	63	144	20		
1,2-Dichloropropane	8260B	Solid	ug/Kg	0.96	5	76	132	20		
1,3,5-Trimethylbenzene	8260B	Solid	ug/Kg	0.58	5	72	128	20		
1,3-Dichlorobenzene	8260B	Solid	ug/Kg	0.91	5	83	122	20		
1,3-Dichloropropane	8260B	Solid	ug/Kg	0.93	5	78	127	20		
1,4-Dichlorobenzene	8260B	Solid	ug/Kg	0.89	5	84	121	20		
2,2-Dichloropropane	8260B	Solid	ug/Kg	1.3	5	67	134	20		
2-Butanone (MEK)	8260B	Solid	ug/Kg	4.2	5	50	150	30		
2-Chlorotoluene	8260B	Solid	ug/Kg	1	5	63	137	20		
2-Hexanone	8260B	Solid	ug/Kg	1.7	5	69	140	20		
4-Chlorotoluene	8260B	Solid	ug/Kg	0.77	5	76	123	20		
4-Methyl-2-pentanone (MIBK)	8260B	Solid	ug/Kg	3	5	68	134	20		
Acetone	8260B	Solid	ug/Kg	4.1	5	46	167	20		

STL Chicago
Method Limit Report

Project: Secor - Remedial Design SE Rockford Area 9/10
Date: 3/17/03

Method Description	Analytical Method	Test Matrix	Units	MDL	Lab RL	LCL	UCL	RPD	SLL	SUL
Benzene	8260B	Solid	ug/Kg	0.66	5	72	128	20		
Bromobenzene	8260B	Solid	ug/Kg	0.71	5	81	123	20		
Bromochloromethane	8260B	Solid	ug/Kg	0.99	5	68	129	20		
Bromodichloromethane	8260B	Solid	ug/Kg	0.68	5	74	128	20		
Bromoform	8260B	Solid	ug/Kg	0.91	5	78	132	20		
Bromomethane	8260B	Solid	ug/Kg	2.9	5	48	127	20		
Carbon disulfide	8260B	Solid	ug/Kg	2	5	23	138	20		
Carbon tetrachloride	8260B	Solid	ug/Kg	0.83	5	67	127	20		
Chlorobenzene	8260B	Solid	ug/Kg	0.91	5	83	125	20		
Chloroethane	8260B	Solid	ug/Kg	1.6	5	59	163	20		
Chloroform	8260B	Solid	ug/Kg	0.62	5	73	135	20		
Chloromethane	8260B	Solid	ug/Kg	0.94	5	45	141	20		
cis-1,2-Dichloroethene	8260B	Solid	ug/Kg	1.2	5	68	148	20		
cis-1,3-Dichloropropene	8260B	Solid	ug/Kg	0.79	5	80	124	20		
Dibromochloromethane	8260B	Solid	ug/Kg	0.69	5	77	127	20		
Dibromomethane	8260B	Solid	ug/Kg	0.69	5	70	130	20		
Dichlorodifluoromethane	8260B	Solid	ug/Kg	0.75	5	43	121	20		
Ethylbenzene	8260B	Solid	ug/Kg	1.1	5	79	123	20		
Hexachlorobutadiene	8260B	Solid	ug/Kg	1	5	66	127	20		
Isopropylbenzene	8260B	Solid	ug/Kg	0.75	5	77	118	20		
m&p-Xylenes	8260B	Solid	ug/Kg	2.1	10	79	123	20		
Methylene chloride	8260B	Solid	ug/Kg	1.8	5	58	143	20		
Methyl-tert-butyl-ether (MTBE)	8260B	Solid	ug/Kg	0.64	5	61	132	20		
Naphthalene	8260B	Solid	ug/Kg	1	5	65	132	20		
n-Butylbenzene	8260B	Solid	ug/Kg	0.84	5	65	138	20		
n-Propylbenzene	8260B	Solid	ug/Kg	0.86	5	77	124	20		
o-Xylene	8260B	Solid	ug/Kg	0.93	5	80	123	20		
p-Isopropyltoluene	8260B	Solid	ug/Kg	0.68	5	74	126	20		
sec-Butylbenzene	8260B	Solid	ug/Kg	0.81	5	77	128	20		
Styrene	8260B	Solid	ug/Kg	1	5	85	126	20		
tert-Butylbenzene	8260B	Solid	ug/Kg	0.78	5	79	124	20		
Tetrachloroethene	8260B	Solid	ug/Kg	0.67	5	75	129	20		
Toluene	8260B	Solid	ug/Kg	1	5	75	125	20		
trans-1,2-Dichloroethene	8260B	Solid	ug/Kg	0.94	5	58	139	20		
trans-1,3-Dichloropropene	8260B	Solid	ug/Kg	0.84	5	75	134	20		
Trichloroethene	8260B	Solid	ug/Kg	0.59	5	75	129	20		
Trichlorofluoromethane	8260B	Solid	ug/Kg	0.71	5	57	135	20		

Method Description	Analytical Method	Test Matrix	Units	MDL	Lab RL	LCL	UCL	RPD	SLL	SUL
Vinyl chloride	8260B	Solid	ug/Kg	0.74	5	58	140	20		
Surrogate										
1,2-Dichloroethane-d4 (surr)	8260B	Solid	ug/Kg						50	145
4-Bromofluorobenzene (surr)	8260B	Solid	ug/Kg						60	140
Dibromofluoromethane (surr)	8260B	Solid	ug/Kg						60	140
Toluene-d8 (surr)	8260B	Solid	ug/Kg						66	141
Method: Volatile Organics (8260B)										
1,1,1,2-Tetrachloroethane	8260B	High/MeOH	ug/Kg	25.5	100	74	120	30		
1,1,1-Trichloroethane	8260B	High/MeOH	ug/Kg	16.5	100	69	133	30		
1,1,2,2-Tetrachloroethane	8260B	High/MeOH	ug/Kg	18.5	100	70	126	30		
1,1,2-Trichloroethane	8260B	High/MeOH	ug/Kg	31.5	100	67	133	30		
1,1-Dichloroethane	8260B	High/MeOH	ug/Kg	13.5	100	68	119	30		
1,1-Dichloroethene	8260B	High/MeOH	ug/Kg	14	100	44	143	30		
1,1-Dichloropropene	8260B	High/MeOH	ug/Kg	18.5	100	65	134	30		
1,2,3-Trichlorobenzene	8260B	High/MeOH	ug/Kg	49	100	68	117	30		
1,2,3-Trichloropropane	8260B	High/MeOH	ug/Kg	49	100	64	118	30		
1,2,4-Trichlorobenzene	8260B	High/MeOH	ug/Kg	41.5	100	61	117	30		
1,2,4-Trimethylbenzene	8260B	High/MeOH	ug/Kg	23	100	69	122	30		
1,2-Dibromo-3-chloropropane	8260B	High/MeOH	ug/Kg	22.5	100	56	102	30		
1,2-Dibromoethane (EDB)	8260B	High/MeOH	ug/Kg	25.5	100	69	122	30		
1,2-Dichlorobenzene	8260B	High/MeOH	ug/Kg	17	100	76	125	30		
1,2-Dichloroethane	8260B	High/MeOH	ug/Kg	21.5	100	64	115	30		
1,2-Dichloroethene (total)	8260B	High/MeOH	ug/Kg	29	100	60	139	30		
1,2-Dichloropropane	8260B	High/MeOH	ug/Kg	17.5	100	70	122	30		
1,3,5-Trimethylbenzene	8260B	High/MeOH	ug/Kg	19.5	100	66	125	30		
1,3-Dichlorobenzene	8260B	High/MeOH	ug/Kg	23	100	75	119	30		
1,3-Dichloropropane	8260B	High/MeOH	ug/Kg	23.5	100	71	118	30		
1,4-Dichlorobenzene	8260B	High/MeOH	ug/Kg	20.5	100	76	127	30		
2,2-Dichloropropane	8260B	High/MeOH	ug/Kg	11.5	100	41	131	30		
2-Butanone (MEK)	8260B	High/MeOH	ug/Kg	51	100	40	125	30		
2-Chlorotoluene	8260B	High/MeOH	ug/Kg	40.5	100	62	134	30		
2-Hexanone	8260B	High/MeOH	ug/Kg	52	100	50	116	30		
4-Chlorotoluene	8260B	High/MeOH	ug/Kg	23	100	66	131	30		
4-Methyl-2-pentanone (MIBK)	8260B	High/MeOH	ug/Kg	37.5	100	54	119	30		
Acetone	8260B	High/MeOH	ug/Kg	29	100	34	143	30		
Benzene	8260B	High/MeOH	ug/Kg	14	100	67	122	30		
Bromobenzene	8260B	High/MeOH	ug/Kg	27.5	100	74	133	30		

Method Description	Analytical Method	Test Matrix	Units	MDL	Lab RL	LCL	UCL	RPD	SLL	SUL
Bromochloromethane	8260B	High/MeOH	ug/Kg	24.5	100	60	124	30		
Bromodichloromethane	8260B	High/MeOH	ug/Kg	19	100	66	128	30		
Bromoform	8260B	High/MeOH	ug/Kg	18	100	70	123	30		
Bromomethane	8260B	High/MeOH	ug/Kg	10.5	100	36	164	30		
Carbon disulfide	8260B	High/MeOH	ug/Kg	20.5	100	21	124	30		
Carbon tetrachloride	8260B	High/MeOH	ug/Kg	16.5	100	59	127	30		
Chlorobenzene	8260B	High/MeOH	ug/Kg	22	100	80	125	30		
Chloroethane	8260B	High/MeOH	ug/Kg	20	100	33	207	30		
Chloroform	8260B	High/MeOH	ug/Kg	18	100	61	129	30		
Chloromethane	8260B	High/MeOH	ug/Kg	23.5	100	55	129	30		
cis-1,2-Dichloroethene	8260B	High/MeOH	ug/Kg	17	100	64	144	30		
cis-1,3-Dichloropropene	8260B	High/MeOH	ug/Kg	22.5	100	68	123	30		
Dibromochloromethane	8260B	High/MeOH	ug/Kg	19	100	70	119	30		
Dibromomethane	8260B	High/MeOH	ug/Kg	22.5	100	67	121	30		
Dichlorodifluoromethane	8260B	High/MeOH	ug/Kg	12	100	29	135	30		
Ethylbenzene	8260B	High/MeOH	ug/Kg	22.5	100	78	128	30		
Hexachlorobutadiene	8260B	High/MeOH	ug/Kg	38.5	100	63	126	30		
Isopropylbenzene	8260B	High/MeOH	ug/Kg	20	100	67	133	30		
m&p-Xylenes	8260B	High/MeOH	ug/Kg	50	200	76	133	30		
Methylene chloride	8260B	High/MeOH	ug/Kg	20	100	57	129	30		
Methyl-tert-butyl-ether (MTBE)	8260B	High/MeOH	ug/Kg	30.5	100	47	126	30		
Naphthalene	8260B	High/MeOH	ug/Kg	38	100	51	158	30		
n-Butylbenzene	8260B	High/MeOH	ug/Kg	18.5	100	64	118	30		
n-Propylbenzene	8260B	High/MeOH	ug/Kg	27.5	100	69	130	30		
o-Xylene	8260B	High/MeOH	ug/Kg	23.5	100	74	127	30		
p-Isopropyltoluene	8260B	High/MeOH	ug/Kg	23.5	100	68	129	30		
sec-Butylbenzene	8260B	High/MeOH	ug/Kg	20.5	100	69	139	30		
Styrene	8260B	High/MeOH	ug/Kg	28.5	100	80	129	30		
tert-Butylbenzene	8260B	High/MeOH	ug/Kg	13.5	100	71	125	30		
Tetrachloroethene	8260B	High/MeOH	ug/Kg	23	100	75	125	30		
Toluene	8260B	High/MeOH	ug/Kg	18	100	72	123	30		
trans-1,2-Dichloroethene	8260B	High/MeOH	ug/Kg	13.5	100	66	138	30		
trans-1,3-Dichloropropene	8260B	High/MeOH	ug/Kg	19.5	100	60	115	30		
Trichloroethene	8260B	High/MeOH	ug/Kg	21.5	100	70	123	30		
Trichlorofluoromethane	8260B	High/MeOH	ug/Kg	19.5	100	59	145	30		
Vinyl chloride	8260B	High/MeOH	ug/Kg	18	100	61	135	30		
Surrogate										

STL Chicago
Method Limit Report

Project: Secor - Remedial Design SE Rockford Area 9/10
Date: 3/17/03

Method Description	Analytical Method	Test Matrix	Units	MDL	Lab RL	LCL	UCL	RPD	SLL	SUL
1,2-Dichloroethane-d4 (surr)	8260B	High/MeOH	ug/Kg						43	139
4-Bromofluorobenzene (surr)	8260B	High/MeOH	ug/Kg						57	124
Dibromofluoromethane (surr)	8260B	High/MeOH	ug/Kg						64	132
Toluene-d8 (surr)	8260B	High/MeOH	ug/Kg						70	128
Method: Jet Fuel-4 (8015D)										
Jet Fuel #4	8015B	Water	mg/L	0.125	0.125	31	103	20		
Surrogate	8015B	Water	mg/L							
2-Fluorobiphenyl (surr)	8015B	Water	mg/L						25	129
o-Terphenyl (surr)	8015B	Water	mg/L						37	159
Method: Jet Fuel-4 (8015D)										
Jet Fuel #4	8015B	Soil	mg/kg	4.2	4.2	50	150	20		
Surrogate	8015B	Soil	mg/kg							
2-Fluorobiphenyl (surr)	8015B	Soil	mg/kg						33	115
o-Terphenyl (surr)	8015B	Soil	mg/kg						34	168

Notes:

MDLs will vary based on annual performance.

RLs will vary based on sample volume/size; dilution factors; dry weight reporting (soils) and annual MDL determinations.

Lower/Upper Control Limits (LCL/UCL) are listed for the LCS and MS/MSD for Organics; LCS limits for TCLP are listed, however, MS limits (post-extraction spikes) are 50-150%.

For Method 8260B, the laboratory will only control the analysis on the highlighted/italicized LCS compounds - not the entire compound list.

ATTACHMENT B
QAPP ADDENDUM FOR THE AS/SVE PILOT TEST
LABORATORY STANDARD OPERATING PROCEDURES

SECOR Project NO.: 13UN.02072.01.0001

July 3, 2003

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: CANISTER CLEANING AND PREPARATION

(SUPERSEDES: KNOX-SC-0001, Revision 3)

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Technical Specialist

Approved By: Marilyn Allen 10/31/01
Quality Assurance Manager

Approved By: Barry Lee Clark 10-26-01
Environmental, Health and Safety Coordinator

Approved By: [signature] 10-26-01
Laboratory Director

1. Purpose

1.1. This standard operating procedure defines the procedure and quality assurance procedures necessary to clean and certify Summa™ canisters for air monitoring.

1.2. This procedure is applicable to all Summa™ canisters used for air monitoring.

2. Responsibilities

2.1. It is the responsibility of the group/team leader to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

3. Safety

3.1. Procedures shall be carried out in a manner that protects the health and safety of all associates.

3.2. Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. VITON gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]

3.3. Exposure to chemicals will be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent, and waste containers will be kept closed unless transfers are being made.

3.4. The preparation of all standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

3.5. All work must be stopped in the event of a known, or potential compromise to the health or safety of an associate. The situation must be reported **immediately** to a laboratory supervisor.

4. Procedure

4.1. General Metal Work, Inc. Oven System

4.1.1. Any high-level canisters (canisters with TICs or target compounds greater than 1 ppm) must be precleaned by inserting a dip tube into the canister and flushing it with inert gas for at least 5 minutes.

4.1.2. Any previously-cleaned canisters on the system need to be removed.

4.1.3. Collect the canisters that have been released for cleaning from the "dirty" shelf.

4.1.4. Attach the cans to the lines of the cleaning system and place them in the oven.

NOTE: Be sure that every spot of the cleaning system is filled, or that an unused spot is capped.

4.1.5. Turn on the oven and gas flow.

4.1.6. Plug in the vacuum pump.

4.1.7. Move the interval regulator switch to "M2" and watch as the system comes under vacuum.

4.1.8. Observe that the pump reaches its normal operating vacuum. If it does not, take corrective action such as leak checking or searching for restrictions in the vacuum line.

4.1.9. Move the interval regulator switch to the middle and pause for a second or two, then move the interval regulator switch to "M1" and watch as the system is pressurized.

4.1.9.1. If the system pressure is too low, increase the flow at the regulator.

4.1.9.2. If the system pressure is too high (> 20 psi), totally release the flow regulator and move the switch back to "M2." Move the interval regulator switch back to "M1" and repressurize the system using the system regulator at 15 to 20 psi.

4.1.10. Move the interval regulator switch to the middle and press START/RESET.

4.1.11. Open the canister valves. The system will operate now automatically.

4.1.12. After at least 6 hours, turn off the oven and move the interval regulator switch to "M2."

4.1.13. Press the START/RESET switch and wait until the system is totally evacuated.

4.1.14. Turn off the gas flow, pump, oven heat and interval regulator.

4.1.15. While cans are in an evacuated state, fill the cold trap 1/3 full with liquid nitrogen. After filling the cold trap, plug in the high vacuum pump, Pirani gauge and vacuum sentry. Open the solenoid valve on the cold trap and turn the Pirani gauge on. The cans are now in the final vacuum stage. When the cans are less than 3 torr, close the canister valves, solenoid valve and turn off the pump, vacuum sentry and Pirani gauge. The cans are now ready for leak checks and blank check analysis.

4.2. Entech 3000 Cleaning Oven System

4.2.1. Any high level canister (canisters with TIC's or target compounds greater than 1 ppm) must be precleaned by inserting a dip tube into the canister and flushing it with inert gas for 5 minutes.

4.2.2. Any previously cleaned canisters on the system need to be removed.

4.2.3. Collect the canisters that have been released for cleaning from the "dirty" shelf.

4.2.4. Attach the cans to the lines of the cleaning system and place them in the oven.

NOTE: Be sure that every spot of the cleaning system is filled or that an unused spot is capped.

4.2.5. Turn on the oven and gas flow.

4.2.6. Plug in the vacuum pump located in the mechanical room.

4.2.7. Set the control panel as follows:

Cycles on C
Pump 1 on 8
Fill on 8.

4.2.8. Put the mode select from standby to pump 1. Observe that the pump reaches its normal operating vacuum. If it does not, take corrective action such as leak checking or searching for restrictions in the vacuum line.

4.2.9. Set the mode select back to standby, then to the fill mode.

4.2.10. If the system pressure is too low, increase the flow of the regulator.

4.2.11. If the system pressure is too high (>20 psi), set the mode back to standby, then pump 1 to release pressure. Set the mode to standby, then fill; adjust the pressure regulator until you have an 15-20 psi operating pressure.

4.2.12. Set the mode to standby, then auto.

4.2.13. Open the canister valves. The system will now operate automatically.

4.2.14. After at least 6 hours, turn off the ovens and gas flow, set the mode to standby, then pump 1.

4.2.15. Once the system is under vacuum, set the mode back to standby. Plug in the high vacuum pump, fill the cold trap 1/3 full, plug in the vacuum sentry and set the mode to pump 2. The cans are now in the final vacuum stage. When the cans are less than 3 torr, close the canister valves, set the mode back to standby and unplug the high vacuum pump and the vacuum sentry. The cans are now ready for removal from the system, leak checks and blank check analysis.

4.3. Leak Testing Canisters

4.3.1. One can from each batch will be pulled for blank check analysis. Preparing a blank consists of spiking the can with 40 microliters of deionized water. The can is filled to a positive pressure of 15 psig. The can is then sent to the GC/MS lab for blank check analysis. For a canister blank check to be considered acceptable, all target compounds must be less than the requested reporting limit.

4.3.2. At least 18 hours after the high vacuum system is turned off, a vacuum reading is taken on each canister. Each canister in a cleaning batch should have approximately the same vacuum as the other canisters in the batch. The reading is taken to assure that the canisters are holding a vacuum. All readings are recorded in a laboratory notebook, with canister ID number.

4.3.3. Canisters with gross leaks (greater than 3 torr) are removed and set aside for maintenance or repair. Once repaired, the canisters are recleaned and rechecked for leaks.

4.3.4. Cans with pressure less than 3 torr but greater than 2X that of the canister with the lowest pressure in the batch should be set aside and rechecked after approximately 24 hours. If the recheck reading is greater than 120% of the initial reading, the canister is set aside for maintenance or repair.

4.4. Blank Checks

4.4.1. Once the cans have been analyzed and returned, the blank check data is stored in a fire-rated file cabinet. The cans are then stamped on the ID tag with the date they were certified clean. The cans are then released to be used in the field for sample collection. If the blank comes back dirty (i.e., the blank check results fail to meet acceptance criteria), the blank and the entire batch of cans is put back through the entire process of cleaning and blank checking.

5. Definitions

5.1. None.

6. Appendices

6.1. References

6.1.1. STL Quality Management Plan (current revision).

6.1.2. Compendium Method TO14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa™ Passivated Canister Sampling and Gas Chromatographic Analysis," U.S. EPA, May 1988.

6.1.3. "SIS Grab Sampling Canisters: User Information/Instruction Sheet," Specific Instrumentation Specialists, Moscow ID.

6.1.4. Instruction Manual, HPS Series 315 Pirani Gauge Micro Controller.

6.1.5. KNOX-MS-0001, "VOA Canister Analysis", latest revision.

6.2. Interferences

6.2.1. Landfill gas and highly contaminated canisters (those with target analytes and tentatively identified compounds (TIC's) greater than 1 ppm) may not be adequately cleaned with the standard procedure and may require an additional cleaning step.

6.3. Preservation and Holding Time

Container Type	Preservative	Holding Time
Summa™ Canister	None	None

6.4. Required Equipment

NOTE: A schematic of the canister cleaning systems is illustrated in Figure 1. Item numbers on the figure follow the items listed below.

6.4.1. Oil-less vacuum pump, capable of evacuating canisters to at least 30 mm Hg absolute (Item No. 1 in Figure 1).

6.4.2. High vacuum pump, Alcatel, Model 2004A or equivalent (No. 2).

6.4.3. Vacuum manifold, stainless steel, with connections for up to 10 and 16 canisters (No. 3).

6.4.4. Vacuum/Pressure gauge, capable of measuring between 30 inches Hg negative pressure and 60 psig (No. 4).

6.4.4.1. The calibration of the vacuum/pressure gauge shall be verified annually. The vacuum reading for the low calibration check must be within $\pm$ 0.05 Torr.

6.4.5. General Metal Work, Inc. Oven System, capable of holding up to ten canisters, able to maintain a minimum of 150°C (No. 5).

6.4.6. Solenoid valve, SMC Model NVS-3125-0209D, or equivalent (No. 6).

6.4.7. Humidifier, six-L canister modified to hold water (No. 7).

6.4.8. Cold Trap (No. 8)

6.4.9. Pirani Gauge, HPS Model 315 or equivalent (No. 9).

6.4.10. Nitrogen Tank (No. 10).

6.4.11. Control Panels, Gralab Model 451 or Entech Model 3000, or equivalent (No. 11).

6.4.12. Vacuum Sentry, PP Model 51X002106B or equivalent (No. 12).

6.4.13. Entech 3000 Cleaning Oven System, capable of holding up to four canisters, able to maintain a minimum of 150°C (No. 13). (Note: Four units are represented in Figure 1)

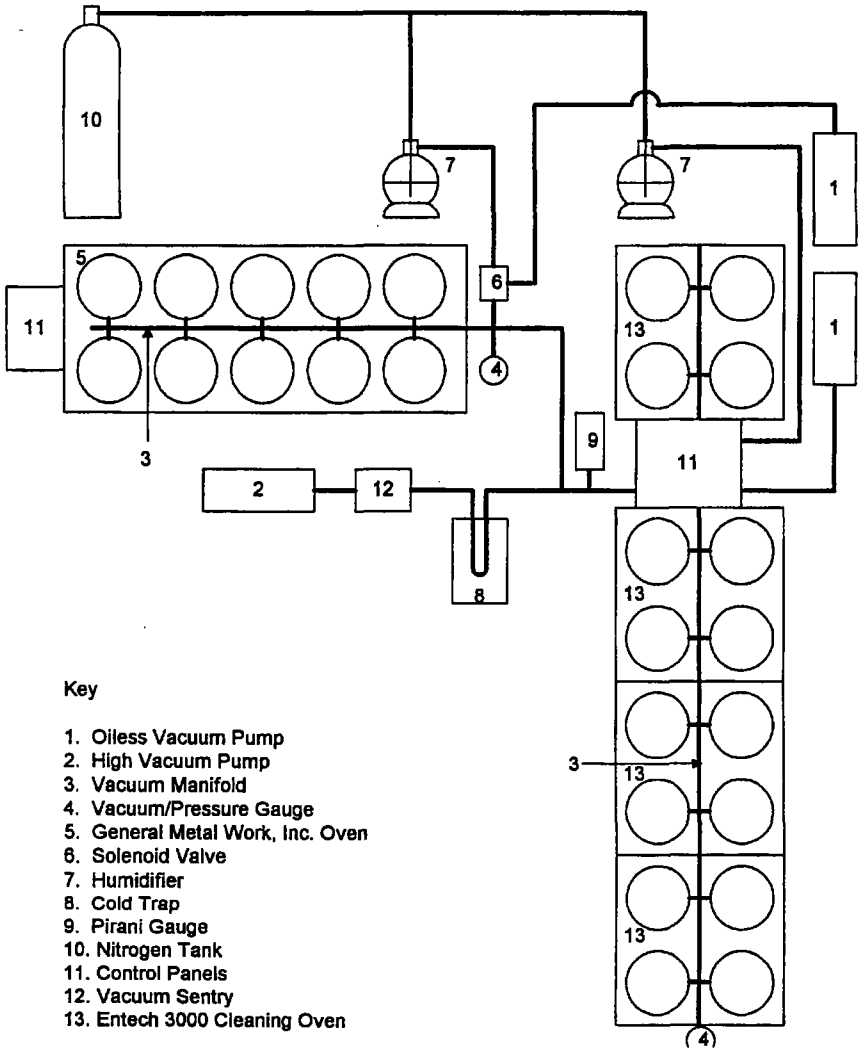
6.5. Reagents/Standards

6.5.1. Air, high purity, total hydrocarbon content less than 0.05 ppm.

6.5.2. Helium or nitrogen, high purity, 99.995% or better.

6.5.3. Water, deionized.

Figure 1: Schematic of the canister cleaning system



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SOP No.: KNOX-MS-0001
Revision No.: 3
Revision Date: 3/19/02
Implementation Date: **3/19/02**

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: VOA CANISTER ANALYSIS

(SUPERSEDES: KNOX-MS-0001, Revision 2)

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Approved By: 3/19/02
Laboratory Director

1. Scope and Application

1.1. The purpose of this Standard Operating Procedure (SOP) is to define the procedures and quality control necessary to analyze samples collected in "SUMMA™ passivated" stainless steel canisters.

1.2. This procedure is applicable to the analysis of ambient air, indoor air, landfill gases and other gaseous samples. It is based on EPA Methods TO-14 and TO-15.

1.3. Responsibilities to perform this procedure in the lab are as follows:

Position	Responsibilities
Analyst	- Prepares and analyzes samples - Summarizes/assembles data package - Reviews the data package
Team/Group Leader	- Schedules/assigns analyses - Reviews data package

2. Summary of Method

2.1. Microscale Purge and Trap (MSPT): A precisely measured aliquot is removed from the canister and concentrated on a cryogenic trap. The cryogenic trap is desorbed. Polar and nonpolar compounds are quantitatively transferred to a subambient Tenax™ trap. Most of the water remains on the Cryotrap and CO_2 passes through the Tenax trap and is vented. The Tenax™ trap is thermally desorbed to the on-column cryofocuser. Sample components are separated by temperature programmed gas chromatography and detected with a quadrupole mass spectrometer.

2.2. The compounds analyzed by this method are listed in Tables 1, 2 and 3.

3. Definitions

3.1. Canister - a stainless steel container, typically 6-liter volume, equipped with a stainless steel shut-off valve, suitable for use from vacuum to 40 psig.

3.2. SUMMA™ Passivation - a proprietary treatment process used to deactivate stainless steel surfaces. It produces a pure chrome/nickel oxide surface that features a high level of inertness.

3.3. Absolute pressure - pressure measured with reference to absolute zero pressure, expressed as kpa, mmHg, or psia.

3.4. Gauge pressure - pressure above atmospheric pressure as measured by a standard gauge. Zero gauge pressure is equal to ambient atmospheric pressure, expressed as mmHg, inches Hg, or psig.

3.5. Polar compound - Oxygen-containing compound capable of forming hydrogen bonds in water; compound having significant solubility in water.

4. Interferences

4.1. Only compounds having both a similar mass spectrum and GC retention time would be expected to interfere in the method. The most common occurrence of this would be with structural isomers.

4.2. Large concentrations of water, methane, or carbon dioxide may limit the size of the aliquot that can be effectively cryotrapped. This may elevate the quantitation limits obtainable for samples of this type.

5. Safety

5.1. Procedures shall be carried out in a manner that protects the health and safety of all associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. VITON gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, methylene chloride and vinyl chloride.

5.3.2. Chemicals known to be **flammable** are methanol, acetonitrile, hexane, acetone and methylene chloride.

5.4. Exposure to chemicals will be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent, and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of all standards and reagents and glassware cleaning procedure that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6. All work must be stopped in the event of a known, or potential compromise to the health or safety of an associate. The situation must be reported **immediately** to a laboratory supervisor.

6. Equipment and Supplies

6.1. Canisters, 6- 15-, and 33-liter sizes, preferably equipped with two valves and integral vacuum/pressure gauge, Scientific Instrumentation/Specialists, Moscow, ID, or equivalent.

6.2. Static gas dilution bottles (SGDB), nominally 2000 ml, with mininert valves, Tekmar Co., Cincinnati, OH, or equivalent.

6.3. Syringes, liquid, 50 µL and 10 µL, and gas-tight, 500 µL, 1000 µL, 2.5 mL, 50 mL, 500 mL, all side port needle, Hamilton, Inc., Reno, NV, or equivalent.

6.4. Mercury barometer, Baxter Scientific Co., Obetz, OH, or equivalent.

6.5. Gas Chromatograph/Mass Spectrometer System, Model XLE or 5100, Finnigan MAT, San Jose, CA, or equivalent.

6.6. Fused silica capillary column, 60 m x 0.32 1µm, film DB-5, J&W Scientific, Folsom, CA or equivalent.

6.7. Vacuum pump, oilless, Model 726.3 TTP, KNF Newberger, Princeton, NJ, or equivalent.

6.8. Canister concentrator system, Model 7000, Entech Co., Simi Valley, CA with a Model 7016, 16-position auto sampler maniold.

6.9. Zero air generator, capable of delivering air with no analytes present at the reporting limit.

6.10. Test gauge, 0 to 30 in. Hg, Jay Instrument Co., Cincinnati, Ohio (NIST certified by Jay Instruments).

6.11. Test gauge 0-60 psi, Jay Instrument Co., Cincinnati, Ohio (NIST certified by Jay Instruments).

7. Reagents and Standards

7.1. Helium, ultra high purity, 99.999+%, Air Products, or equivalent.

7.2. Liquid nitrogen, 22 psig, Air Products, or equivalent.

7.3. Nitrogen, ultra high purity, Air Products or equivalent

7.4. Internal/Surrogate Standard: bromochloromethane, 1,4-difluorobenzene, d5-chlorobenzene, d4-1, 2-dichloroethane, d8-toluene (all at 40 ppb) and bromofluorobenzene (at 20 ppb) in nitrogen, 2000 psig, Scott Specialty Gases, Troy, MI, or equivalent.

7.4.1. Approximately 40 µL of boiled deionized water is injected through an 11 mm septum (inserted into a 1/4 inch nut) into a clean evacuated 15-liter canister. The canister is allowed to stand for at least 20 minutes to allow all the water to evaporate from the valve area.

7.4.2. A sufficient volume (approximately 30 liters) from the internal/surrogate standard cylinder is transferred to the 15-liter summa canister to produce the working internal/surrogate standard at a pressure of approximately 15 psig.

7.4.3. The working internal/surrogate standard may be used as long as the pressure in the canister remains above ambient pressure.

7.5. Gaseous Standards, target compounds, 300 ppb v/v, vendor-certified high-pressure aluminum cylinders (except those compounds listed in sections 1.4 and 1.5).

7.5.1. The expiration date for the gaseous standards contained in the certified high-pressure aluminum cylinders has not been specified by the vendor. No significant degradation in response been observed for over 9 years. Due to this stability, a nominal expiration date of 20 years has been assigned to this standard. This is subject to ongoing monitoring of target analytes through second source standards.

7.6. Calibration Verification Standard stock cylinder, TO-14 list compounds, 100 ppb v/v, vendor-certified high-pressure aluminum cylinder (see table 1). Spectra Gases or equivalent.

7.6.1.1. The calibration verification standard stock cylinder may be used for 20 years from date of certification or until the vendor assigned expiration date, whichever is earlier.

7.7. Standard grade neat compounds of hexachloro-cyclobutadiene (HCB) and naphthalene, 99+% or of known purity, Chem Service, West Chester, PA; or equivalent.

7.7.1. Naphthalene/Hexachlorobutadiene (HCB) Stock Standard: Approximately 3.5 mg of naphthalene is weighed into a quartz crucible small enough to be dropped into a SGDB. The crucible is introduced into the SGDB and the bottle is capped with a mininert valve. Approximately 4.5 µL of HCB is added to the SGDB using a 10 µL syringe. The exact weight/volume to be added is calculated from the volume of the SGDB such that adding 5 milliliters from the SGDB to the working standard yields a concentration of 50 ppb(v/v) of HCB and Naphthalene in the working standard. The SGDB is placed in an oven at 60°C for at least 24 hours.

7.8. Prepared Standard, polar compounds, vendor certified mix containing methanol, ethyl ether, acetone, acrylonitrile, vinyl acetate, 2-butanone, 1-butanol, 4-methyl-2-pentanone, 2-hexanone, methyl-tert-butyl ether, acrolein, and acetonitrile, Ultra Scientific, North Kingstown, RI or equivalent.

7.8.1. Polar Stock Standard: Approximately 30 µL of the polar standard mix is injected into a SGDB via a 50 µL syringe. The exact volume to be added is calculated from the volume of the SGDB such that adding 10 mL from the SGDB to the working standard yields a concentration of 200 ppb (v/v) for

methanol and 100 ppb(v/v) for the other polar compounds in the working standard.

7.9. Additional Standards: Neat materials, not contained in the certified cylinders, can be added to a SGDB either individually or as a mix.

7.9.1. If the desired compound is a gas at room temperature, a measured volume should be injected into an evacuated summa canister and pressurized. For example, 5 mL of the gas are added to an evacuated 6 liter summa canister. The canister is pressurized with ultra-high purity (UHP) nitrogen to exactly 3 atm gauge pressure. A 7.2 mL injection of this standard to the 15 liter canister will result in a concentration of 50 ppb v/v in the final canister standard.

7.9.2. If the desired compound is a liquid or solid at room temperature, the volume of each liquid to be added to the SGDB should be back calculated so that the final concentration in the canister standard is exactly 50 ppb v/v. For example, if the standard is a liquid with a density of 1 g/mL and a molecular weight of 100 g/mole, and 3 mL of the SGDB will be transferred to the canister, then 4.1 μL of the standard would be added to a 2000 mL SGDB.

7.10. 50 ppb v/v Canister Stock

7.10.1. 100 μL of boiled deionized water is injected through an 11 mm septum (inserted into a 1/4-in. nut) into a clean evacuated 15-liter canister. The canister is allowed to stand for at least 20 minutes to allow all the water to evaporate from the valve area.

7.10.2. 10 mL of the polar stock, 5 mL of the naphthalene/HCB stock, and 3 mL of the SGDB containing the additional compounds (as applicable) are injected through the septum. The canister is then brought up to exactly zero inches gauge pressure with UHP nitrogen.

7.10.3. The barometric pressure is read and 1/3 atmosphere of each high pressure gas standard is added to the 15 liter canister.

7.11. Low Standard Preparation: 1 and 5 ppb v/v calibration point, if needed

7.11.1. 40 μL of boiled deionized water is injected through an 11 mm septum (inserted into a 1/4 inch nut) into a clean evacuated 6-liter canister. The

canister is allowed to stand for at least 20 minutes to allow all the water to evaporate from the valve area.

7.11.2. Three 400 mL aliquots of the 50 ppb (v/v) standard are injected through the septum using the glass and Teflon 0.5 liter syringe.

7.11.3. The barometric pressure is read and 1 atmosphere of UHP nitrogen is added to the 6 liter canister.

7.12. 50 ppb v/v Laboratory Control Standard

7.12.1. 100 µL of boiled deionized water is injected through an 11 mm septum (inserted into a 1/4-in. nut) into a clean evacuated 15-liter canister. The canister is allowed to equilibrate for at least 20 minutes to allow all the water to evaporate from the valve area.

7.12.2. The canister is brought up to exactly zero inches gauge pressure with UHP nitrogen.

7.12.3. The barometric pressure is read and 1 atmosphere of the laboratory control standard stock cylinder is added to the 15 liter canister.

7.13. Approved SGDB and canister stock standards (section 1.7) may be used for 6 months from the date of preparation. Working canister standards may be used for two months from the date of preparation.

7.14. The HCB/naphthalene SGDB is stored at 60°C. Other SGDB and canister standards are stored at room temperature. Mixes and neat compounds are stored between -20 °C and 6°C.

7.15. Approval of Stock Standards

7.15.1. Every six months when the new stock is made, it is analyzed by comparison to the old stock. Alternately, two new stocks may be prepared.

7.15.2. The SGDB standards are analyzed as follows: Humidify two 6 liter canisters with 40 µL of water each, and spike with equal known volumes (typically 5 - 10 mL) of the standards, and bring to an equal final pressure of nominally 15 psig.

7.15.3. The two standards must agree to within 20 percent difference after taking into account nominal volume differences between the two bottles.

7.15.4. Working canister standards are approved for use by analysis versus another 50 ppb v/v canister standard. The acceptance criteria are given in Section 9.

7.15.5. The working LCS canister is approved for use by passing the LCS acceptance criteria. The acceptance criteria are given in Section 9.

8. Sample Collection, Preservation and Storage

Container Type	Preservative	Holding Time
SUMMA canister	None	30 days

9. Quality Control

9.1. Internal/Surrogate Standards

9.1.1. Internal standards and surrogates are added to each analytical standard, blank and sample. The acceptance criteria for each internal standard's area for every analysis must be $\pm$ 40% recovery of the internal standard area from the continuing calibration standard. The acceptance criteria for each internal standard's retention time in every analysis must be within $\pm$ 20 seconds of the internal standard retention time from the continuing calibration standard.

9.1.2. Surrogate recoveries must fall within 70% to 130%.

9.1.3. If the internal standard areas or surrogate recoveries for a sample are outside their limits, the cause is determined. If it is a result of a system problem, then the problem must be corrected and the sample reanalyzed with acceptable results. If it is the result of a matrix effect, the sample must be reanalyzed to confirm this unless the effect is caused by obviously high levels of non-target compounds co-eluting with surrogates or internal standards.

9.2. Initial Calibration and Tune Check

9.2.1. All abundance criteria for BFB must be met using the tune check or the first run of a calibration curve (See Figure 1).

9.2.2. A calibration curve is valid for all target analytes if the relative standard deviation (RSD) is ≤ 30% for each target analyte, with the following allowance: up to two target analytes may have an RSD ≤ 40%.

9.2.3. The area response at each calibration level must be within 40% of the mean area response over the initial calibration range for each internal standard.

9.2.4. The retention time (RT) shift for each of the internal standards at each calibration level must be within 20 seconds of the retention time of the mid-level calibration for each internal standard.

9.2.5. The RT of each target compound must be within 0.5 minutes of the RT of the mid-level standard in the initial calibration.

9.3. Daily Continuing Calibration and Tune Check

9.3.1. All abundance criteria for BFB in Figure 1 must be met using the tune standard or the daily calibration standard.

9.3.2. A mid-level standard (usually 10 ppb) is analyzed as the continuing calibration standard. For all analytes, a percent difference (%D) is calculated using the response factor from the standard and the average response factor from the current initial calibration curve.

9.3.2.1. The continuing calibration standard used may be a different standard from the one used for the initial calibration as long as the standard used contains all target analytes at the same level as the standard used to generate the initial calibration curve.

9.3.3. A continuing calibration standard is acceptable if the %D is within ± 30% for all target analytes with the following allowance: a maximum of four target analytes may have %D of ≤40%.

9.3.4. If the continuing calibration standard does not meet the above criteria, corrective action must be taken and/or a new initial calibration performed unless project specific analytes or client specified QC criteria are met.

9.4. Initial Calibration Verification (ICV) Standard

9.4.1. The ICV is a second source standard containing the TO-14 list compounds at 10 ppb (Table 1) and is analyzed after the five point calibration. For

each analyte, a percent recovery (%R) is calculated using the response factor from the daily continuing calibration standard.

9.4.2. The ICV is valid for all analytes if the %R is between 65% and 135% for each TO-14 list analyte in the ICV. Benzyl chloride ICV acceptance criteria is 20-180%.

9.5. System Blanks

9.5.1. For each 24 hour tune in which samples are analyzed or every 20 samples, whichever is more frequent, an acceptable system blank must be analyzed before samples analysis may begin.

9.5.1.1. A system blank is defined as a sample from a cleaned canister, humidified with 100 uL of water and filled with UHP nitrogen nominally to 15 psig.

9.5.1.2. An acceptable system blank is one with all target analytes less than or equal to the laboratory reporting limit (see Tables 1, 2 and 3).

9.5.2. If a system blank does not meet the above criteria, then the blank must be reanalyzed or a new blank made and analyzed with acceptable results.

9.6. Laboratory Control Standard (LCS)

9.6.1. The LCS is defined as a working standard made by the same method as analytical standards, using the same source materials. It is used to assess analytical control of this procedure. The LCS is analyzed every 24 hour tune or every 20 samples, whichever is more frequent.

9.6.2. All non-polar analytes in the LCS must be within 70-130% recovery with the allowance of up to two non-polar analytes having 60-140% recovery. All polar analytes in the LCS must be within 60-140% recovery with the allowance of up to two polar analytes having 45-155% recovery.

9.6.3. If the above criteria cannot be met, a new standard must be prepared.

9.7. Canister Blank Checking

9.7.1. From each cleaned lot of canisters, a canister is selected, humidified with 40 µL clean water, and pressurized nominally to 15 psig with UHP

nitrogen. (See SOP KNOX-SC-0001, current revision, "Canister Cleaning and Preparation").

9.7.2. A blank check is analyzed within 24 hours of a valid tune check and calibration. Alternately, a blank check may be analyzed within 24 hours of a valid tune check/single mid-point standard.

9.7.3. A blank check passes if all target analytes are present at less than the reporting limit.

9.7.4. If a blank check canister does not pass, the can may be re-analyzed. If the acceptance criteria is still not met, the entire lot of canisters must be re-cleaned, and a blank check from the re-cleaned lot must pass.

9.8. Duplicate Analysis

9.8.1. A duplicate is analyzed with every 20 samples. It is not reported unless specifically requested.

9.8.2. The acceptance criteria for the duplicate analysis is:
$\leq$ 30% RPD for non-polar compounds that are greater than 5 times the RL
$\leq$ 40% RPD for polar compounds that are greater than 5 times the RL
No criteria for methanol and n-butanol.

10. Calibration and Standardization

10.1. Instrument Conditions

10.1.1. The mass spectrometer is leak checked by scan for air and water on a daily basis per instructions given by the manufacturer (for example, see the instrument manuals).

10.1.2. Mass assignments of the mass spectrometer are checked and adjusted using perfluorotributylamine (PFTBA FC43).

10.1.3. The mass spectrometer is tuned to meet the criteria for BFB (see Figure 1).

10.1.4. The mass spectrometer is adjusted to minimize noise (see instrument manufacturer instruction manuals).

10.1.5. See Tables 1, 2 and 3 for suggested quantitation ions.

10.2. Initial Calibration

10.2.1. A five-point calibration curve is analyzed for all analytes. The dynamic range of the curve is generally 0.2 ppb v/v to 30 ppb v/v for most analytes. The concentration of the low standard of the calibration should be at or below the reporting limit.

10.2.2. The BFB spectrum of the first standard must meet the criteria listed in Figure 1. Alternatively, a tune standard may be analyzed prior to the five point curve in which the BFB spectrum meets the criteria listed in Figure 1. Whichever analysis is used as the tune standard establishes the beginning of the daily 24 hour clock.

10.2.3. The initial calibration curve must meet all criteria outlined in Section 3.2

10.2.4. If the curve is acceptable and there is time remaining in the 24 hour tune, blanks and samples may be analyzed. The concentrations in the samples and blanks are calculated using the response factors from the mid-range standard (10 ppb) from the initial calibration curve.

10.3. Initial Calibration Verification (ICV)

10.3.1. The ICV is a second source standard containing the TO-14 list compounds at 10 ppb (Table 1) and is analyzed after the five point calibration. The ICV is valid for all analytes if the %R is between 65% and 135% for each TO-14 list analyte in the ICV. Benzyl chloride ICV acceptance criteria is 20-180%. See section 3.4.2.

10.4. Daily Continuing Calibration Check

10.4.1. On each day in which samples are to be analyzed, a daily continuing calibration check (CCC) standard must be analyzed for all target analytes. The CCC is analyzed at a concentration of 10 ppb v/v for most target analytes.

10.4.2. The BFB spectrum of the CCC must meet the criteria listed in Figure 1. Alternatively, a tune standard may be analyzed prior to the continuing calibration check standard in which the BFB spectrum meets the criteria listed in Figure 1. The analysis that is used as the tune standard establishes the beginning of the daily 24 hour clock.

10.4.3. The CCC is acceptable if it meets all criteria outlined in Section 9.3.

10.4.4. If the CCC does not meet the criteria outlined in Section 9.3, then corrective action must be taken and/or a new initial calibration performed.

11. Procedure

11.1. Following a successful initial or continuing calibration and prior to analysis of actual samples an acceptable system blank must be analyzed (see section 9.5). Following a successful system blank analysis, actual sample analysis may begin.

11.1.1. The desired sample size of each sample to be analyzed is determined. The standard aliquot size is 500 mL.

11.1.2. The pressure of each sample canister is checked. If the pressure is above 15 psig, the excess pressure is vented.

11.1.3. Each sample name, volume (aliquot), method, and manifold position are loaded into the Entech M 7000 data system name list.

11.1.4. The automated flush function is used to sweep each manifold line in the name list with helium.

11.1.5. The cans are then securely tightened onto the tree with the canister valves closed.

11.1.6. An automated leak check is run on each position. A hard copy of the leak check results is included with the daily calibration package.

11.1.7. If all positions pass the leak check, the canister valves are opened.

11.1.8. A name list identical to the Entech name list is written to the GC/MS auto sampler program. After the batch number and method are added to the miscellaneous information, the amount injected, the can number and a notation for in-can or serial dilution are added as well.

11.1.9. The Entech autosampler is started and the GC/MS autosampler program is started. (Note: The scan and GC descriptors are initiated by the GC/MS autosampler procedure.)

11.1.10.100 ml of the surrogate/internal standard is added by the Entech concentrator to the stage one cryogenic trap prior to sample introduction.

11.1.11. The analyses proceed automatically for each name in the Entech autosampler program.

11.2. Instrument Dilutions

11.2.1. Volumes of 10 to 1000 mL may be analyzed by the instrument. The standard aliquot is 500 mL, which equals a dilution factor of one.

11.2.2. If an analyte found in the sample is over the curve by less than a factor of ten, then the aliquot size of the sample may be reduced to a volume as low as 10 mL. This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.

11.2.3. If an instrument dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 5 ppb (v/v) measured against the daily continuing calibration check, unless there are significant amounts of non-target compounds present.

11.3. Water addition

11.3.1. The analyst should be aware that humidity plays an important role in the recovery of certain target compounds, particularly polar compounds, and should be prepared add humidity to canisters where appropriate. The addition of water helps to stabilize the behavior of these compound, which might otherwise interact with the interior surface of the summa canister or with the stainless-steel lines of the sample manifold.

11.3.2. Since it is not practical to know the relative humidity of all canisters received at the laboratory, the analyst should assume that canisters are received at approximately 80 percent relative humidity. When making canister dilutions (see Sections 11.4, 11.5, and 11.6), the analyst should attempt to preserve the relative humidity of canisters at a level that will minimize recovery loss due to low canister relative humidity.

11.3.3. Under normal laboratory conditions, a 6 liter summa canister at ambient pressure will have a relative humidity of 100 percent if approximately 100 uL of water is evaporated in the canister.

11.3.3.1. The minimum relative humidity at which canisters containing polar analytes can be analyzed before polar target recovery is negatively affected is approximately 20 - 30 percent.

11.3.3.2.The minimum relative humidity at which canisters containing nonpolar analytes can be analyzed before nonpolar target recovery is negatively affected is approximately 10 percent.

11.4. Canister Dilutions

11.4.1. Samples that have an initial pressure of less than 0 psig upon receipt must be pressurized to a pressure greater than 0 psig prior to analysis.

11.4.1.1.Measure the initial pressure of the canister using an NIST traceable, certified vacuum gauge.

11.4.1.2.The analyst may elect to add 40 uL of deionized water to the canister through a septum sealed nut (See Section 11.3 for guidance on addition of water.).

11.4.2. Next, fill the canister with UHP nitrogen to the desired pressure. This pressure should be between 0 and 40 psig.

11.4.3. The final pressure is measured using an NIST traceable, certified gauge.

11.4.4. The canister is allowed to equilibrate for approximately one hour. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig.

11.4.5. The barometric pressure, the aliquot volume, initial pressure and final pressure are recorded in a laboratory notebook.

11.4.6. This canister may be further diluted, if necessary, by any dilution methods.

11.5. High Levels Sample

11.5.1. High-level samples, for example, are those containing ppm levels of volatile organic compounds.

11.5.2. The original sample canister must have a pressure of between 0 to 15 psig. If the pressure is less than 0 psig, then proceed to Section 11.3. If the canister is greater than 15 psig, then it must be bled down to about 15 psig. A septum cap is attached to the sample canister and a 50-mL gas-tight syringe is purged with UHP nitrogen. A septum cap is attached to a clean evacuated 6-liter canister (the dilution canister).

11.5.3. The syringe is inserted into the septum cap of the canister containing the sample and the canister valve is opened. The syringe is purged twice with sample and vented. The desired volume is then withdrawn and transferred into the dilution canister. 40 µL of deionized water is also added to the dilution canister (See Section 11.3 for guidance on addition of water.). The dilution canister is then pressurized using UHP nitrogen.

11.5.4. The final pressure is measured in the new canister using a NIST traceable, certified gauge.

11.5.5. The barometric pressure, the aliquot volume and final canister pressure are recorded in a laboratory notebook. The serial dilution factor is calculated.

11.5.6. If a high level dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 5 ppb (v/v) measured against the daily continuing calibration check, unless there are significant amounts of non-target compounds present. It is imperative that non-target analytes not contaminate the analytical system.

11.5.7. This new canister may be further diluted, if necessary, by any dilution method. The final dilution factor is the product of all the dilution factor for the sample.

11.6. In-canister Dilutions

11.6.1. If an analyte found in the sample is over the curve by greater than a factor of ten, an in-canister dilution may be performed.

11.6.2. The canister is bled to ambient pressure. The analyst may elect to add 40 µL of deionized water to the canister prior to pressurization (See Section 11.3 for guidance on addition of water.)

11.6.3. Next, the canister is pressurized to the desired pressure. This pressure should be between 10 and 40 psig.

11.6.4. The final pressure is measured using an NIST traceable, certified gauge.

11.6.5. The canister is allowed to equilibrate for one hour. If the canister was pressurized to greater than 15 psig, pressure should be released from the canister to bring the pressure below 15 psig.

11.6.6. The barometric pressure and the initial and final pressures are recorded in a laboratory notebook.

11.6.7. If an in-canister dilution is performed to bring one or more analytes within the curve, the analyte having the highest concentration should not be diluted to less than 5 ppb (v/v) measured against the daily continuing calibration check, unless there are significant amounts of non-target compounds present. Care should be taken to avoid over-dilution for in-canister dilutions since the original sample is affected.

11.6.8. This canister can be further diluted, if necessary, by any dilution method. This dilution factor is multiplied with all other dilution factors for this sample to obtain the final dilution factor.

11.7. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry sample size or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified.

11.8. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. Data Analysis and Calculations

12.1. Calculation legend:

12.1.1. A = amount of neat compound, µL

12.1.2. CB = concentration in SGDB, µg/mL

12.1.3. CC = concentration in canister, ppb v/v

12.1.4. CS = concentration in mix, µg/µL

12.1.5. C_x = the value determined by vendor certification analyses is used in the following calculations, ppb v/v (300 ppb nominal)

12.1.6. d = density of neat compound, g/mL

12.1.7. DF = dilution factor, unitless

12.1.8. Fv_{can} = final volume in a pressurized canister, liters

12.1.9. GC = gas constant at 25°C and standard pressure, 24.45 nL/n mole

12.1.10. MW = molecular weight, ng/n mole

12.1.11. P_B = barometric pressure

12.1.12. P_F = final pressure, units specified

12.1.13. P_I = initial pressure, units specified

12.1.14. P_T = transfer pressure, units specified

12.1.15. P_x = pressure in X = inches, psia or mmHg

12.1.16. TK = temperature in Kelvin

12.1.17. Tv_x = transfer volume, liters or µL

12.1.18. V_{bottle} = volume of static gas dilution bottle, mL

12.1.19. V_{mix} = volume of mix, µL

12.2. Calculations:

12.2.1. Final Canister Volume

$$FV = \frac{Canister\ size(L)\ x\ P_F(mm\ Hg\ Abs)}{P_B(mm\ Hg\ Abs)}$$

12.2.2. $P_{mm\ Hg}$ = P inches x 25.4

12.2.3. P inches = P_{psi} * 2.036

12.2.4. $P_{mm}\ Hg = P_{psi} \times 51.7149$

12.3. Polar stock:

12.3.1. $$CS\ \mu g / uL = \frac{A * d * 1000}{V_{mix}}$$

12.3.2. $$CB\ \mu g / mL = \frac{CS * TV,\ \mu L}{V_{bottle}}$$

12.4. Polar concentration in target dilution standard

$$CC,\ ppb\ v/v = \frac{TV,\ \mu L\ *\ CB \times GC}{MW\ *\ FV}$$

12.5. Hexachlorobutadiene/naphthalene stock

12.5.1.

$$CB_{HCB},\ \mu g / mL = \frac{2.5\ \mu L\ *\ d\ *\ 1000}{V_{bottle}}$$

12.5.2.

$$CB_{NAPHTH},\ \mu g / mL = \frac{2\ mg\ *\ 1000}{V_{bottle}}$$

12.6. Concentration of HCB/naphthalene in primary target standard.

$$CC,\ ppb\ v/v = \frac{0.8829 * TV,\ mL\ *\ CB \times 1000\ *\ GC}{FV\ *\ MW}$$

where 0.8829 is a temperature correction factor.

12.7. Concentration of Cylinder Standards: Concentration of Nonpolar Analytes in Primary Target Standard

$$CC,\ ppb\ v/v = \frac{(P_T - P_I,\ psi)(Cx)}{(P_F,\ psi + PB,\ psi)}$$

12.8. Target Dilution Standard (CC is the concentration of the Primary Target Standard).

$$CC,\ ppb\ v/v = \frac{(P_T - P_I)(CC)}{(P_F + PB,\ psi)}$$

12.9. Dilution Factor of original sample canisters

$$DF = \frac{P_{f\ (mm\ Abs)}}{P_{i\ (mm\ Abs)}} \times \frac{Sample\ volume\ injected}{500\ ml}$$

12.9.1. Serial Dilution Factor

$$DF = FV/TV$$

12.10. Response Factor (RF)

$$RF = \frac{Ax * Cis}{Ais * Cx}$$

where:

x	=	area of the characteristic ion for the target compound.
Ais	=	area of the characteristic ion for the internal standard.
Cx	=	amount of the target compound.
Cis	=	amount of the internal standard.

12.11. Average Response Factor (ARF)

$$ARF = \frac{RF_1 + RF_2 + ... + RF_n}{n}$$

where:
n = the number of calibration points

12.12. Standard deviation of the ARF:

$$S = \sqrt{\frac{\sum_i^n (ARF - RF_n)^2}{n-1}}$$

12.13. Relative standard deviation (RSD) of the ARF:

$$RSD = \frac{S}{ARF} * 100\%$$

12.14. Continuing Calibration Check: Percent deviation (% D) of the daily RF values as compared with the initial ARF values:

$$\%D = \frac{|RF - ARF|}{ARF} * 100\%$$

12.15. Laboratory Control Sample percent recovery (%R):

$$\%R = \frac{FoundAmount, ppb}{SpikeAmount, ppb} * 100\%$$

12.16. Duplicate relative percent difference (RPD):

$$RPD = \frac{|A_1 - A_2|}{\overline{A}} x\ 100\%$$

where:
A_1 = amount determined in first analysis
A_2 = amount determined in second analysis
A = average determination, $(A_1 + A_2)/2$

12.17. Sample Quantitation: The amount of target compound detected is determined using the daily RF values:

$$Amount = \frac{Ax * Cis * DF}{Ais * RF}$$

12.18. Unit conversions

12.18.1.

$$Amount, \mu g / m^3 = \frac{Amount, ppb * MW}{GC}$$

12.18.2.

$$Amount, ppm\ v / v = amount, \frac{ppb\ v / v}{1000}$$

12.19. Quantitation of Unknowns

12.19.1. If required, nontarget peaks are reported with probable identifications as Tentatively Identified Compounds (TICs). These are quantitated using the nearest internal standard and assuming a response factor of 1; correction for dilution factor is also made. Search criteria are those in the STL Knoxville SOP KNOX-MS-0014, Tentatively Identified Compounds (TICs).

12.20. Estimated results (less than the reporting limits listed in Tables 1, 2 and 3) are not normally calculated for this procedure.

13. Method Performance

13.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. Pollution Prevention

14.1. All attempts will be made by laboratory personnel to minimize the use of solvents when performing this procedure.

15. Waste Management

15.1. Waste generated in this procedure must be segregated and disposed according to the facility hazardous waste procedures.

16. References

16.1. Compendium Method TO-14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA™ Passivated Canister Sampler and Gas Chromatographic Analysis," U.S. EPA 600/4-89/017, June 1988.

16.2. Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GCMS)", U.S. EPA 625/R-96/010b, January 1997.

16.3. Compendium Method IP-1A, "Determination of Volatile Organic Compounds (VOCs) in Indoor Air: Stainless Steel Canisters," U.S. EPA Draft, September 1989.

16.4. "Standard Operating Procedure for the Preparation and Use of Standard Organic Gas Mixtures in a Static Gas Dilution Bottle," Berkeley, R.E.; Swanson, D.H.; Bumgarner, J.E.; Environmental Monitoring Systems Laboratory, U.S. EPA, RTP, NC.

16.5. "S.I.S. Grab Sampling Containers: User Information/Instruction Sheet," Scientific Instrumentation Specialists, Moscow, ID.

16.6. "Operator's Manual, Entech Model 7000 Concentrator," Entech Co., Simi Valley, CA.

16.7. "Automated Cryogenic Preconcentration and Gas Chromatographic Determination of Volatile Organic Compounds in Air", McCleny, W.A.; Pleil, J.D., Holdren, M.W., Smith, R.N., Analytical Chemistry; 1984, 56 2947-2270.

16.8. "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air", Riggen, R.M., EPA-600/4-84-041, April 1984.

16.9. Supplement to EPA/600/4-84/041: "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air", Riggen, R.M., Winbury, W.T., Tilly, in the reference standard, EPA-600/4-87/006.

16.10. "U.S. EPA Contract Laboratory Program Statement of Work for Organic Analysis", Multi-Media, Multi-Concentration Rev. 2/88.

16.11. "Canister Sampling and Analysis of VOC's in Air", Entech Instruments, Inc., 1998 (Winter/Spring 1998 Seminar Series).

16.12. STL Quality Management Plan (current revision).

17. Miscellaneous

17.1. Other SOPs cross-referenced in this SOP: KNOX-SC-0001, "Canister Cleaning and Preparation", latest revision.

17.2. Modification from the referenced methods

17.2.1. The TO-15 tune criteria were not used in this procedure. The tune criteria listed in TO-14 is tighter and thus was used in this procedure.

17.2.2. The continuing calibration listed in this procedure allows up to 4 target analytes with a %D of $\leq$ 40%.

17.2.3. This procedure also allows for the use of BFB in the continuing calibration to meet the tune criteria.

17.2.4. This procedure requires that all target analytes in the initial calibration must be within 0.5 minutes of the analyte RT in the mid-level initial calibration standard. TO-15 specifies that all target analytes must be within 0.06 RRT units of the mean RRT for the initial calibration. If the RT of the first internal standard is greater than 8.3 minutes the criteria are equivalent.

17.2.5. This procedure uses purified nitrogen in place of zero humid air specified in the reference methods.

17.2.6. This procedure requires that the RT shift for the internal standards at each calibration level must be within 20 seconds of the RT of the mid-level calibration for each internal standard. TO-15 specifies that the comparison

is made to the mean RT over the initial calibration range for each internal standard.

17.3. List of tables and figures referenced in the body of the SOP:

17.3.1. Table 1: Target Analytes - TO-14 Compounds

17.3.2. Table 2: Target Analytes - Other Nonpolar Compounds

17.3.3. Table 3: Target Analytes - Other Polar Compounds

17.3.4. Figure 1: BFB Tuning Criteria

17.3.5. Figure 2: Example of a Data Review Checklist

17.3.6. Figure 3: Flow Chart

Table 1: Target Analytes - TO-14 Compounds

CAS NUMBER	METHOD TO-14 COMPOUND	REPORTING LIMIT (ppb, v/v)	MOLECULAR WEIGHT (ng/n mole)	RETENTION TIME [a] (minutes)	SUGGESTED ION
75-71-8	Dichlorodifluoromethane (b)	0.2	120.91	2.83	85
76-14-2	1,2-Dichlorotetrafluoroethane (c)	0.2	170.93	2.97	135
74-87-3	Chloromethane	0.5	50.49	2.97	52
75-01-4	Vinyl Chloride	0.2	62.5	3.11	62
74-83-9	Bromomethane	0.2	94.94	3.42	94
75-00-3	Chloroethane	0.2	64.52	3.53	64
75-69-4	Trichlorofluoromethane (d)	0.2	137.38	3.96	101
75-35-4	1,1-Dichloroethene	0.2	96.94	4.50	96
76-13-1	1,1,2-Trichlorotrifluoroethane (e,f)	0.2	187.38	4.64	101
75-09-2	Methylene Chloride (f)	0.5	84.93	4.77	84
76-34-3	1,1-Dichloroethane	0.2	98.96	5.73	63
156-59-2	cis-1,2-Dichloroethene	0.2	96.94	6.52	96
67-66-3	Chloroform	0.2	119.38	6.81	83
71-55-6	1,1,1-Trichloroethane	0.2	133.41	7.67	97
56-23-5	Carbon Tetrachloride	0.2	153.82	8.22	117
71-43-2	Benzene	0.2	78.12	8.20	78
107-06-2	1,2-Dichloroethane	0.2	98.96	7.77	62
79-01-6	Trichloroethene	0.2	131.39	9.44	130
78-87-5	1,2-Dichloropropane	0.2	112.99	9.40	63
10061-01-5	cis-1,3-Dichloropropene	0.2	110.97	10.83	75
108-88-3	Toluene	0.2	92.15	11.87	91
10061-02-6	trans-1,3-Dichloropropene	0.2	110.97	11.72	75
79-00-5	1,1,2-Trichloroethane	0.2	133.41	11.97	97
127-18-4	Tetrachloroethene	0.2	165.83	13.32	129
106-93-4	1,2-Dibromoethane	0.2	187.87	13.22	107
108-90-7	Chlorobenzene	0.2	112.56	14.32	112
100-41-4	Ethylbenzene	0.2	106.17	14.65	91
IT5-30-5	m/p-Xylene (g)	0.2	106.17	14.83	91
95-47-6	o-Xylene	0.2	106.17	15.39	91
100-42-5	Styrene	0.2	104.16	15.33	104
79-34-5	1,1,2,2-Tetrachloroethane	0.2	167.85	15.73	83
108-67-8	1,3,5-Trimethylbenzene	0.2	120.19	16.78	105 or 120
95-63-6	1,2,4-Trimethylbenzene	0.2	120.19	17.22	105
541-73-1	1,3-Dichlorobenzene	0.2	147.01	17.49	146
106-46-7	1,4-Dichlorobenzene	0.2	147.01	17.58	146
100-44-7	Benzyl Chloride	0.2	126.59	17.57	91
95-50-1	1,2-Dichlorobenzene	0.2	147.01	17.95	146
120-82-1	1,2,4-Trichlorobenzene	0.2	181.46	19.75	180
87-68-3	Hexachlorobutadiene	0.2	260.76	20.10	225

a) Approximate Times
b) Freon 12
c) Freon 114
d) Freon 11
e) Freon 113
f) This is a common laboratory solvent
g) m-xylene and p-xylene coelute

Table 2: Target Analytes - Other Nonpolar Compounds

CAS NUMBER	OTHER NON-POLAR COMPOUNDS	REPORTING LIMITS (ppb, v/v)	MOLECULAR WEIGHT (ng/n mole)	RETENTION TIME [a] (minutes)	SUGGESTED ION
75-45-6	Chlorodifluoromethane (b)	0.2	86.47	2.78	51
106-97-8	n-Butane	0.2	58.13	3.18	43
106-99-0	1,3-Butadiene	0.2	54.09	3.17	54
109-66-0	Pentane	0.5	72.15	4.14	41
75-15-0	Carbon Disulfide	0.2	76.14	4.89	76
107-05-1	3-Chloropropene	0.2	76.53	4.78	39
156-60-5	trans-1,2-Dichloroethene	0.2	96.94	5.40	96
110-54-3	n-Hexane	0.2	86.18	6.19	56
110-82-7	Cyclohexane	0.5	84.16	8.19	69
142-82-5	n-Heptane	0.2	100.21	9.32	43
74-95-3	Dibromomethane	0.2	173.85	9.52	93
75-27-4	Bromodichloromethane	0.2	163.86	9.68	83
111-65-9	n-Octane	0.2	114.13	12.81	85
124-48-1	Dibromochloromethane	0.2	208.29	12.87	129
111-84-2	Nonane	0.2	128.26	15.33	57
75-25-2	Bromoform	0.2	252.75	15.28	173
98-82-8	Cumene	0.2	120.2	16.00	105
103-65-1	n-Propylbenzene	0.2	120.19	16.54	91
124-18-5	Decane	0.2	142.29	17.10	57
98-83-9	alpha-Methylstyrene	0.2	118.18	17.01	118
1120-21-4	n-Undecane	0.2	156.32	18.45	57
112-40-3	n-Dodecane	0.2	170.34	19.55	57
91-20-3	Naphthalene	0.2	128.19	19.90	128

96) Approximate Times
96) Freon 22

Table 3: Target Analytes – Other Polar Compounds

CAS NUMBER	OTHER POLAR COMPOUNDS	REPORTING LIMITS (ppb, v/v)	MOLECULAR WEIGHT (ng/n mole)	RETENTION TIME [a] (minutes)	SUGGESTED ION
67-56-1	Methanol	10	32.04	3.11	31
60-29-7	Ethyl Ether	0.5	74.12	4.26	31
67-64-1	Acetone	5	58.08	4.09	58
107-13-1	Acrylonitrile	0.5	53.06	4.60	53
108-05-4	Vinyl Acetate	0.5	86.09	5.83	43
78-93-9	2-Butanone	0.5	72.12	6.19	72
71-36-3	1-Butanol	0.5	74.12	8.19	31
108-10-1	4-Methyl-2-Pentanone	0.5	100.16	10.79	43
591-78-6	2-Hexanone	0.5	100.16	12.51	58
1634-04-4	Methyl-t-Butylether	0.5	88.09	5.51	73
107-02-8	Acrolein	0.5	56.06	3.99	56
75-05-8	Acetonitrile	1.0	41.05	4.05	40 (or 41)
96-18-4	1,2,3-Trichlorpropane	0.5	255.5	13.03	110

a) Approximate Times

Figure 1: BFB Tuning Criteria

Mass	Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	Less than 2% of mass 174
174	Greater than 50% of mass 95
175	5 to 9% of mass 174
176	95% to 101% of mass 174
177	5 to 9 % of mass 176

Figure 2: Example Data Review Checklist

STL Knoxville GC/MS Air Initial Calibration Data Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 3

Analysis Date:		Instrument::		ICAL Batch/Scan Name:		Scanned ☐

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd ✔
1. Did BFB meet tune criteria?					
2. Were all standards injected within 24 hr of BFB?					
3. Is the second source analysis of a reference standard within limits? (65-135% R; 20-180% for benzyl alcohol)					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Were at least 5 levels of each compound analyzed?					
6. Is %RSD for all target analytes ≤ 30%? (with up to 2 compounds with RSD ≤ 40%)					
7. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
8. Have alternate hits/manual integrations been verified as correct and are correct RFs listed in ICAL summary?					
9. Was ICAL summary form processed using correct result files? (Analyst and 2nd reviewer should compare 2-3 RFs from each standard quan report to ICAL summary.)					
10. Are the ICAL start and end dates/times correct on ICAL summary?					
11. Elution order checked on isomeric pairs? • cis- and trans- isomers • ethyl benzene / m/p-xylene / o-xylene • 1,3,5-trimethylbenzene / 1,2,4-trimethylbenzene / 4-ethyl toluene • 1,3- , 1,4- , and 1,2-dichlorobenzene • vinyl acetate / hexane • trichlorofluoromethane / 1,1,2-trichlorotrifluoroethane • dichlorodifluoromethane / 1,2-dichlorotetrafluoroethane					
12. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
13. Does the ICAL folder contain complete data in the following order? Data review checklist, a complete runlog, Entech report, ICAL summary, followed by [Quan reports, chromatograms, manual integrations] in increasing sample order, leak check report.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

Figure 2: Example Data Review Checklist (continued)

STL Knoxville GC/MS Air Continuing Calibration Review / Narrative Checklist
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 3

Analysis Date:		CCAL Batch/ Scan Name:		Instrument:		ICAL Batch/ Scan Name:		Scanned ☐

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd ✔
1. Did BFB meet tune criteria?					
2. Were all standards injected within 24 hr of BFB?					
3. Did the LCS meet criteria (nonpolar target analytes 70-130%, with up to 2 nonpolars 60-140%; polar target analytes 60-140%, with up to 2 polars 45-155%)?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the CCAL compared to the correct ICAL?					
6. Was a mid-level standard used for CCAL?					
7. Is the %D ≤ 30% for all target analytes? (up to 4 target analytes %D ≤ 40%)					
8. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
9. Have alternate hits/manual integrations been verified as correct and are correct RFs listed in CCAL summary?					
10. Is the first IS documented correctly on the log?					
11. Is the ICAL date & time on the CCAL correct?					
12. Elution order checked on isomeric pairs/coeluters? • cis- and trans- isomers • ethyl benzene / m/p-xylene / o-xylene • 1,3,5-trimethylbenzene / 1,2,4-trimethylbenzene / 4-ethyl toluene • 1,3- , 1,4- , and 1,2-dichlorobenzene • vinyl acetate / hexane • trichlorofluoromethane / 1,1,2-trichlorotrifluoroethane • dichlorodifluoromethane / 1,2-dichlorotetrafluoroethane					
13. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
14. Does the CCAL folder contain **complete** data in the following order: data review checklist, a **complete** runlog, Entech report, tune pass/fail page, m/z list, tune chromatogram, Target CCAL summary, Quan report, chromatogram, manual integrations and leak check report.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

Figure 2: Example Data Review Checklist (continued)

STL Knoxville GC/MS Air Data Review / Narrative Checklist **LOT/Project #_____**
Method: TO-14 and TO-15 - KNOX-MS-0001, Rev 3 **Page 1 of 1**

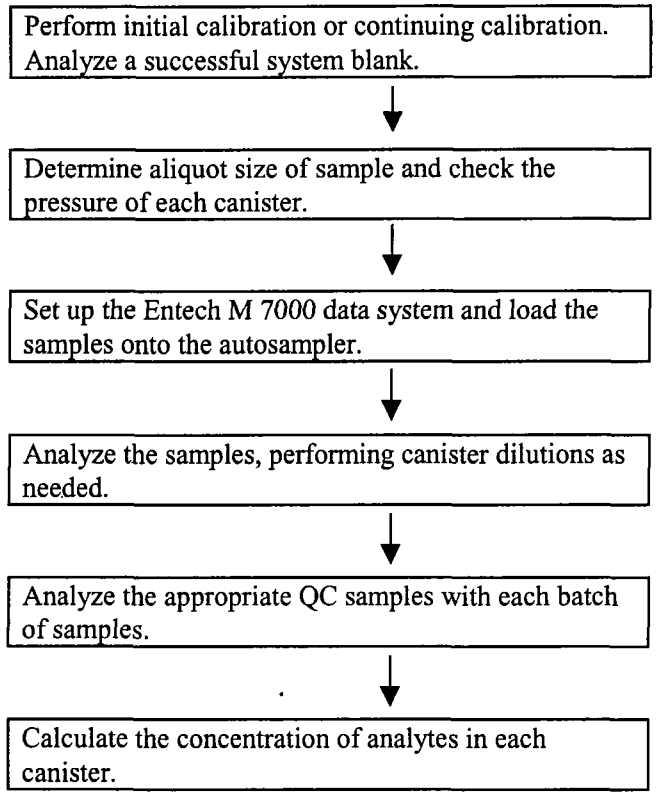
Instrument:		
Scanned File Names:		

Review Items **A. Tune / Continuing Calibration**	N/A	Yes	No	**Why is data reportable?**	2nd ✔
1. Were all samples injected within 24 hr of BFB?					
2. Has a Continuing Calibration Checklist been completed for each analytical batch?					
3. Was the correct CCAL used for quantitation?					
B. CLIENT SAMPLE AND QC SAMPLE Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	
1. Were all special project requirements met?					
2. Were dilution factors/header information verified?					
3. Are surrogates and internal standards within QC limits? (70-130% R for surr.; 60-140%R from CCAL for IS) *If no, list samples/reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____				[sur1] DUP surr. %R demonstrated same effect. [sur2] Reanalysis demonstrated same effect. **[sur5] At client's request, data was flagged as estimated & released without further investigation.*** **[is1] Per client, reanalysis was not performed *** [is2] Reanalysis confirmed a matrix effect.	
4. Were positive hits evaluated using qualitative identification criteria and technical judgement?					
5. Are positive results within calibration range?					
6. For dilutions, is highest concentration hit ≥ 5 ppb? *List samples and reason (e.g.,* **elev1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____				[elev1] Elevated RL for (ANALYTE) due to sample matrix interferences. [elev3] Elevated RLs for all analytes due to difficult sample matrix. [elev5] Elevated RLs for all analytes due to presence of non-target compounds.	
7. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1)Corrected split peak; 2)Unresolved peak; 3)tailing; 4)RT shift; 5)wrong peak selected; 6)other	
8. Have alternate hits/manual integrations been verified as correct?					
9. Final report acceptable? (Results correct, RLs calculated correctly, units correct, surrogate %R correct, appropriate flags used, dilution factor correct, analysis dates correct.)					
10. Was a narrative prepared and all deviations noted?					
C. Preparation QC					
1. System blank run every 24 hours prior to samples?					
2. System blank surrogate recoveries within QC limits (70-130% R) ?				**[mb1] All sample surrogates OK and there is no analyte >RL in samples associated with blank.***	
3. Are all analytes present in the system blank ≤ RL? *If no, list blank ID:* _____ _____ _____				**[mb3] No analyte > RL in associated samples.*** **[mb4] Sample results > 20x higher than blank.** **[mb6]**-Common lab contaminant (methylene chloride/Freon) ≤2x RL.*	
4. DUP done per 20 samples and are all RPDs within limits? (for analytes >5x RL, ≤30 RPD for nonpolars; ≤40 RPD for polars; no criteria for methanol and n-butanol) *If no, list DUP ID:* _____					
D. Other					
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**2nd Level Reviewer:**	**Date:**
Comments:		**Comments:**	

* Such action must be taken in consultation with client.

Figure 3: Flow Chart



ATTACHMENT C
QAPP ADDENDUM FOR THE AS/SVE PILOT TEST
SAMPLE LABELS AND CHAIN OF CUSTODY FORMS

SECOR Project NO.: 13UN.02072.01.0001

July 3, 2003

P.O. Box 1160
Beaver, WV 25813
800-255-3950 • 304-255-3900
Quality Environmental Containers

PROJECT NAME

SAMPLE ID	**SAMPLE DATE**
SAMPLED BY	**SAMPLE TIME**
PRESERVATIVE	___ **GRAB** ___ **COMPOSITE**
ANALYSIS REQUESTED	

P.O. Box 1160
Beaver, WV 25813
800-255-3950 • 304-255-3900
Quality Environmental Containers

PROJECT NAME		TARE WT.
SAMPLE ID	SAMPLE DATE	SAMPLE TIME
SAMPLED BY	PRESERVATIVE	
ANALYSIS REQUESTED	___ GRAB ___ COMPOSITE	

CUSTODY SEAL

DATE _____

SIGNATURE _____

QEC
Quality Environmental Containers
800-255-3950 • 304-255-3900

SEVERN TRENT SERVICES

STL Chicago
2417 Bond Street
University Park, IL 60466
Phone: 708-534-5200
Fax: 708-534-5211

Report To:

Contact: _____
Company: _____
Address: _____
_____
Phone: _____
Fax: _____
E-Mail: _____

To:

Contact: _____
Company: _____
Address: _____
_____
Phone: _____
Fax: _____
PO#: _____ Quote: _____

Shaded Areas For Internal Use ____ of ____

Lab Lot#

Package Sealed	Samples Sealed
Yes No	Yes No
Received on Ice	**Samples Intact**
Yes No	Yes No
Temperature °C of Cooler	

Within Hold Time	Preserv. Indicated
Yes No	Yes No NA
pH Check OK	Res Cl_2 Check OK
Yes No NA	Yes No NA

Sample Labels and COC Agree
Yes No COC not present

Additional Analyses / Remarks

Sampler Name:

Signature:

Project Name:

Project Number:

Project Location:

Lab PM:

Date Required
Hard Copy: ____/____/____
Fax: ____/____/____

Laboratory ID	MS-MSD	Client Sample ID	Sampling Date	Sampling Time	Matrix	Comp/Grab	Refrg #	# / Cont.	Volume	Preserv								

RELINQUISHED BY	COMPANY	DATE	TIME	RECEIVED BY	COMPANY	DATE	TIME
RELINQUISHED BY	COMPANY	DATE	TIME	RECEIVED BY	COMPANY	DATE	TIME

Matrix Key

WW = Wastewater	SE = Sediment
W = Water	SO= Solid
S = Soil	DS = Drum Solid
SL = Sludge	DL = Drum Liquid
MS = Miscellaneous	L = Leachate
OL = Oil	WI = Wipe
A = Air	O = _____

Container Key

1. Plastic
2. VOA Vial
3. Sterile Plastic
4. Amber Glass
5. Widemouth Glass
6. Other

_____

Preservative Key

1. HCl, Cool to 4°
2. H2SO4, Cool to 4°
3. HNO3, Cool to 4°
4. NaOH, Cool to 4°
5. NaOH/Zn, Cool to 4°
6. Cool to 4°
7. None

COMMENTS

Date Received ____/____/____

Courier: **Hand Delivered** ☐

Bill of Lading

196

200

NO POUCH NEEDED.
See back for peel and stick application instructions.

FedEx Express USA Airbill

FedEx Tracking Number 8390 7979 4708

MURRAY

From I.D. No. 0215 | Sender's Copy

1 From *Please print and press hard.*

Date | Sender's FedEx Account Number 2285-4050-1

Sender's Name | Phone (217) 698-7247

Company SECOR INTERNATIONAL INC.

Address 400 N BRUNS LN

Dept./Floor/Suite/Room

City SPRINGFIELD State IL ZIP 62702-4617

2 Your Internal Billing Reference
First 24 characters will appear on invoice.

3 To

Recipient's Name | Phone ( )

Company

Address
To "HOLD" at FedEx location, print FedEx address. We cannot deliver to P.O. boxes or P.O. ZIP codes.

Address

Dept./Floor/Suite/Room

City State ZIP

Try online shipping at fedex.com

By using this Airbill you agree to the service conditions on the back of this Airbill and in our current Service Guide, including terms that limit our liability.

Questions? Visit our Web site at fedex.com
or call 1.800.Go.FedEx® 800.463.3339.

0237686880

4a Express Package Service — *Packages up to 150 lbs.* Delivery commitment may be later in some areas.

- ☐ FedEx Priority Overnight — Next business morning
- ☐ FedEx Standard Overnight — Next business afternoon
- ☐ FedEx First Overnight — Earliest next business morning delivery to select locations
- ☐ FedEx 2Day — Second business day
- ☐ FedEx Express Saver — Third business day

FedEx Envelope rate not available. Minimum charge: One-pound rate

4b Express Freight Service — *Packages over 150 lbs.* Delivery commitment may be later in some areas.

- ☐ FedEx 1Day Freight* — Next business day
- ☐ FedEx 2Day Freight — Second business day
- ☐ FedEx 3Day Freight — Third business day

* Call for Confirmation:

5 Packaging — * Declared value limit $500

- ☐ FedEx Envelope*
- ☐ FedEx Pak* — Includes FedEx Small Pak, FedEx Large Pak, and FedEx Sturdy Pak
- ☐ Other

6 Special Handling — Include FedEx address in Section 3.

- ☐ **SATURDAY Delivery** — Available ONLY for FedEx Priority Overnight and FedEx 2Day to select ZIP codes
- ☐ **HOLD Weekday** at FedEx Location — NOT Available for FedEx First Overnight
- ☐ **HOLD Saturday** at FedEx Location — Available ONLY for FedEx Priority Overnight and FedEx 2Day to select locations

Does this shipment contain dangerous goods? One box must be checked.

- ☐ No
- ☐ Yes — As per attached Shipper's Declaration
- ☐ Yes — Shipper's Declaration not required
- ☐ Dry Ice — Dry Ice, 9, UN 1845 ____ x ____ kg

Dangerous Goods (including Dry Ice) cannot be shipped in FedEx packaging.

☐ Cargo Aircraft Only

7 Payment *Bill to:* — Enter FedEx Acct. No. or Credit Card No. below.

- ☐ Sender — Acct. No. in Section 1 will be billed.
- ☐ Recipient
- ☐ Third Party
- ☐ Credit Card
- ☐ Cash/Check

FedEx Acct. No. / Credit Card No. | Exp. Date

Total Packages	Total Weight	Total Declared Value†	
		$ .00	FedEx Use Only

†Our liability is limited to $100 unless you declare a higher value. See back for details.

8 Release Signature *Sign to authorize delivery without obtaining signature.*

By signing you authorize us to deliver this shipment without obtaining a signature and agree to indemnify and hold us harmless from any resulting claims.

447

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PULL AND RETAIN THIS COPY BEFORE AFFIXING TO THE PACKAGE.

ATTACHMENT D
QAPP ADDENDUM FOR THE AS/SVE PILOT TEST
LIST OF ACRONYMS

SECOR Project NO.: 13UN.02072.01.0001

July 3, 2003

LIST OF ACRONYMS/ABBREVIATIONS

AOC	Administrative Order on Consent
ARARs	Applicable or Relevant and Appropriate Requirements
AS	Air Sparging
ASTM	American Standards for Testing Materials
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act (Superfund)
COC	Chain of Custody
CLP	Contract Laboratory Program
CRDL	Contract Required Detection Limits
CRQL	Contract Required Quantitation Limits
CRL	Central Regional Laboratory
DCF	Document Control Format
DRO	Diesel Range Organics
DQO	Data Quality Objective
EAPM	Early Action Project Manager
EMSL	Environmental Monitoring and Support Laboratory
FSP	Field Sampling Plan
FSS	Field Services Section
IEPA	Illinois Environmental Protection Agency
MDLs	Method Detection Limits
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NIST	National Institute of Standard Technology
NPL	National Priorities List
QA/QC	Quality Assurance/Quality Control
QAMP	Quality Assurance Management Plan
QAPP	Quality Assurance Project Plan
QLs	Quantitation Limits
PARCC	Precision, Accuracy, Representativeness, Completeness, and Comparability
PDI	Pre-Design Investigation
PE	Performance Evaluation Sample
RAS	Routine Analytical Services
RCRA	Resource Conservation and Recovery Act
RI/FS	Remedial Investigation/Feasibility Study
RD/RA	Remedial Design/Remedial Action
RPD	Relative Percent Difference
RPM	Remedial Project Manager
SAP	Sampling and Analysis Plan
SARA	Superfund Amendments and Reauthorization Act
SAS	Special Analytical Services
SER	Southeast Rockford
SF	Superfund
SMC	Sample Management Coordinator
SOP	Standard Operating Procedure
SOW	Statement of Work
SVE	Soil Vapor Extraction
SW-846	Test Methods for Evaluating Solid Waste
TAL	Target Analytes List
TCL	Target Compound List
TSA	Technical System Audit
USEPA	United States Environmental Protection Agency

ATTACHMENT E
QAPP ADDENDUM FOR THE AS/SVE PILOT TEST
STANDARD OPERATING PROCEDURES

SECOR Project NO.: 13UN.02072.01.0001

July 3, 2003

ATTACHMENT E
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MANUFACTURERS OPERATING INSTRUCTIONS FOR THE USE OF A HACH DIGITAL TITRATOR (OR EQUIVALENT)

Carbon Dioxide

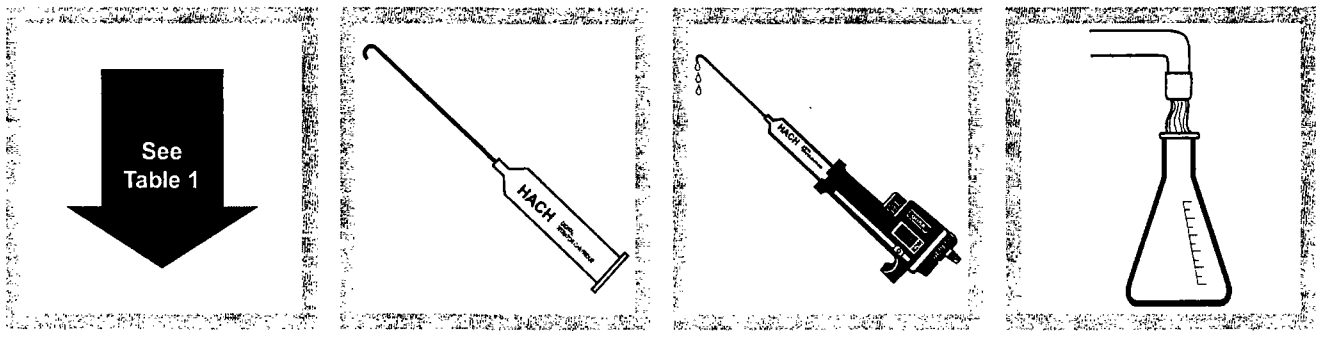
Method 8205

Digital Titrator Method Using Sodium Hydroxide (10 to 1000 mg/L as CO_2)

Digital Titrator

Scope and Application: For water and seawater

- For added convenience when stirring, use the TitraStir apparatus (Cat. No. 19400-00, -10).
- For more accurate results, check the calibration of the Erlenmeyer flask. Fill a graduated cylinder with the sample volume of deionized water. Pour the water into the Erlenmeyer flask and mark the proper level with a wax pencil or permanent marker.
- *Four drops of Phenolphthalein Indicator Solution (Cat. No. 162-32) can be substituted for the Phenolphthalein Indicator* Powder Pillow.
- Minimize agitation of the sample to avoid loss of carbon dioxide.



1. Select a sample size and a Sodium Hydroxide (NaOH) Titration Cartridge in *Table 1* that correspond to the expected carbon dioxide (CO_2) concentration.

2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.

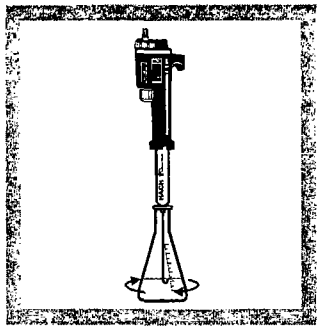
3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

4. Collect a water sample directly into the titration flask by filling to the appropriate mark.

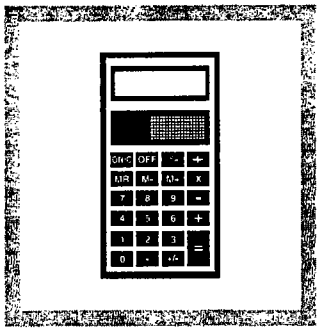
Carbon Dioxide

5. Add the contents of one Phenolphthalein Indicator Powder Pillow and mix.

If a pink color forms, no carbon dioxide is present.



6. Place the delivery tube into the solution and swirl the flask gently while titrating with sodium hydroxide from colorless to a light pink color that persists for 30 seconds (pH 8.3). Record the number of digits required.



7. Calculate:

Total Digits Required x Digit Multiplier = mg/L as CO_2

Table 1

10–50	200	0.3636	14378-01	0.1
20–100	100	0.3636	14378-01	0.2
100–400	200	3.636	14380-01	1.0
200–1000	100	3.636	14380-01	2.0

Interferences

Highly colored or turbid sample may mask the color change of the end point. Use a pH meter (Cat. No. 51700-10) for these samples, titrating to pH 8.3. Other acid components in the sample will be titrated and interfere directly in this determination.

Sodium hydroxide standard solutions tend to lose strength slowly with age and should be checked periodically by titrating a known standard. Check the solution frequently (monthly) by titrating 50 mL of Potassium Acid Phthalate Standard Solution, 100 mg/L CO_2, using Phenolphthalein Indicator Solution. The titration should require 5.00 mL of titrant. If the volume required for this titration is greater than 5.25 mL, discard the sodium hydroxide and replace it with a fresh supply.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples as soon as possible after collection. If immediate analysis is not possible, the samples may be stored for at least 24 hours by cooling to 4 °C (39 °F) or below. Before analysis, warm the samples to room temperature.

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Carbon Dioxide Voluette Ampule Standard for Carbon Dioxide, 10,000 mg/L CO_2.
2. Use a TenSette Pipet (Cat. No. 19700-01) to add 0.1 mL of standard to the sample titrated in step 6. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using additions of 0.2 mL and 0.3 mL. Titrate to the same end point after each addition.
4. Each 0.1 addition of standard should require 50 additional digits of 0.3636 N titrant or five digits of 3.636 N titrant. If these uniform increases do not occur, refer to *Section 3.2.2 Standard Additions* on page *46*.

Summary of Method

Acidity due to carbon dioxide in a sample is titrated with sodium hydroxide to a phenolphthalein end point. Strong acids are assumed to be absent or of insignificant concentration. See *Appendix A, Chemical Procedures Explained.*

Required Reagents (varies with sample characteristics)

Description	Unit	Cat. No.
Carbon Dioxide Reagent Set (about 100 tests)		22727-00
Includes:		
Phenolphthalein Powder Pillows	100/pkg	942-99
Sodium Hydroxide Titration Cartridge, 0.3636 N	each	14378-01
Sodium Hydroxide Titration Cartridge, 3.636 N	each	14380-01
Water, deionized	4 L	272-56

Required Apparatus

Digital Titrator	each	16900-01
Select one or more based on sample concentration:		
Flask, Erlenmeyer, 250-mL	each	505-46
Flask, Erlenmeyer, 125-mL	each	505-43

Required Standards

Carbon Dioxide Standard Solution, Voluette® Ampule, 10,000-mg/L as CO_2, 10-mL	16/pkg	14275-10
Phenolphthalein Indicator Solution, 5-g/L	100 mL MDB	162-32
Potassium Acid Phthalate Standard Solution, 100-mg/L as CO_2	100 mL	2261-42

A-26

MANUFACTURERS OPERATING INSTRUCTIONS FOR THE USE OF A HORIBA U-SERIES WATER QUALITY INSTRUMENT (OR EQUIVALENT)

TO BE PROVIDED TO FIELD PERSONNEL.

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MANUFACTURERS OPERATING INSTRUCTIONS FOR MARK PRODUCTS HELIUM DETECTORS (OR EQUIVALENT)

TO BE PROVIDED TO FIELD PERSONNEL.

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MANUFACTURERS OPERATING INSTRUCTIONS FOR RKI INSTRUMENTS EAGLE ™ MULTI-GAS DETECTOR (OR EQUIVALENT)

TO BE PROVIDED TO FIELD PERSONNEL.

A-29

MANUFACTURERS OPERATING INSTRUCTIONS FOR DWYER THERMAL ANEMOMETER PITOT TUBES PRESSURE GAUGES, AND VACUUM GAUGES (OR EQUIVALENT)

TO BE PROVIDED TO FIELD PERSONNEL.

A-30

MANUFACTURERS OPERATING INSTRUCTIONS FOR SKC DUAL BALL ROTOMETERS (OR EQUIVALENT)

TO BE PROVIDED TO FIELD PERSONNEL.

ATTACHMENT F
QAPP ADDENDUM FOR THE AS/SVE PILOT TEST
LABORATORY ANALYTICAL METHODS

SECOR Project NO.: 13UN.02072.01.0001

July 3, 2003

METHOD 18 - MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY

NOTE: This method is not inclusive with respect to specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3.

NOTE: This method should not be attempted by persons unfamiliar with the performance characteristics of gas chromatography, nor by those persons who are unfamiliar with source sampling. Particular care should be exercised in the area of safety concerning choice of equipment and operation in potentially explosive atmospheres.

1.0 Scope and Application.

1.1 Analyte. Total gaseous organic compounds.

1.2 Applicability.

1.2.1 This method is designed to measure gaseous organics emitted from an industrial source. While designed for ppm level sources, some detectors are quite capable of detecting compounds at ambient levels, e.g., ECD, ELCD, and helium ionization detectors. Some other types of detectors

are evolving such that the sensitivity and applicability may well be in the ppb range in only a few years.

1.2.2 This method will not determine compounds that (1) are polymeric (high molecular weight), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions.

1.3 Range. The lower range of this method is determined by the sampling system; adsorbents may be used to concentrate the sample, thus lowering the limit of detection below the 1 part per million (ppm) typically achievable with direct interface or bag sampling. The upper limit is governed by GC detector saturation or column overloading; the upper range can be extended by dilution of sample with an inert gas or by using smaller volume gas sampling loops. The upper limit can also be governed by condensation of higher boiling compounds.

1.4 Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound.

2.0 Summary of Method.

The major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by flame ionization, photoionization, electron capture, or other appropriate detection principles. The retention times of each separated component are compared with those of known compounds under identical conditions. Therefore, the analyst confirms the identity and approximate concentrations of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation.

3.0 Definitions. [Reserved]

4.0 Interferences.

4.1 Resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming.

4.2 The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen.

4.3 Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately is best dealt with by thorough purging of the GC sample loop between samples.

4.4 To assure consistent detector response, calibration gases are contained in dry air. To adjust gaseous organic concentrations when water vapor is present in the sample, water vapor concentrations are determined for those samples, and a correction factor is applied.

4.5 The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next run (in order to prevent sample carryover).

5.0 Safety.

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method. The analyzer users manual should be consulted for specific precautions to be taken with regard to the analytical procedure.

6.0 Equipment and Supplies.

6.1 Equipment needed for the presurvey sampling procedure can be found in Section 16.1.1.

6.2 Equipment needed for the integrated bag sampling and analysis procedure can be found in Section 8.2.1.1.1.

6.3 Equipment needed for direct interface sampling and analysis can be found in Section 8.2.2.1.

6.4 Equipment needed for the dilution interface sampling and analysis can be found in Section 8.2.3.1.

6.5 Equipment needed for adsorbent tube sampling and analysis can be found in Section 8.2.4.1.

7.0 Reagents and Standards.

7.1 Reagents needed for the presurvey sampling procedure can be found in Section 16.1.2.

7.2 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, an audit sample may be obtained from the appropriate EPA Regional Office or from the responsible enforcement authority.

NOTE: The responsible enforcement autority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

8.0 Sample Collection, Preservation, Storage, and Transport.

8.2 Final Sampling and Analysis Procedure. Considering safety (flame hazards) and the source

conditions, select an appropriate sampling and analysis procedure (Section 8.2.1, 8.2.2, 8.2.3 or 8.2.4). In situations where a hydrogen flame is a hazard and no intrinsically safe GC is suitable, use the flexible bag collection technique or an adsorption technique.

8.2.1 Integrated Bag Sampling and Analysis.

8.2.1.1 Evacuated Container Sampling Procedure. In this procedure, the bags are filled by evacuating the rigid air-tight container holding the bags. Use a field sample data sheet as shown in Figure 18-10. Collect triplicate samples from each sample location.

8.2.1.1.1 Apparatus.

8.2.1.1.1.1 Probe. Stainless steel, Pyrex glass, or Teflon tubing probe, according to the duct temperature, with Teflon tubing of sufficient length to connect to the sample bag. Use stainless steel or Teflon unions to connect probe and sample line.

8.2.1.1.1.2 Quick Connects. Male (2) and female (2) of stainless steel construction.

8.2.1.1.1.3 Needle Valve. To control gas flow.

8.2.1.1.1.4 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent. To deliver at least 1 liter/min.

8.2.1.1.1.5 Charcoal Adsorption Tube. Tube filled with activated charcoal, with glass wool plugs at each end, to adsorb organic vapors.

8.2.1.1.1.6 Flowmeter. 0 to 500-ml flow range; with manufacturer's calibration curve.

8.2.1.1.2 Sampling Procedure. To obtain a sample, assemble the sample train as shown in Figure 18-9. Leak-check both the bag and the container. Connect the vacuum line from the needle valve to the Teflon sample line from the probe. Place the end of the probe at the centroid of the stack or at a point no closer to the walls than 1 m, and start the pump. Set the flow rate so that the final volume of the sample is approximately 80 percent of the bag capacity. After allowing sufficient time to purge the line several times, connect the vacuum line to the bag, and evacuate until the rotameter indicates no flow. Then position the sample and vacuum lines for sampling, and begin the actual sampling, keeping the rate proportional to the stack velocity. As a precaution, direct the gas exiting the rotameter away from sampling personnel. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Record the source temperature, barometric pressure, ambient temperature, sampling flow rate, and initial and final sampling time on the data sheet shown in

Figure 18-10. Protect the Tedlar bag and its container from sunlight. Record the time lapsed between sample collection and analysis, and then conduct the recovery procedure in Section 8.4.2.

8.2.1.2 Direct Pump Sampling Procedure. Follow 8.2.1.1, except place the pump and needle valve between the probe and the bag. Use a pump and needle valve constructed of inert material not affected by the stack gas. Leak-check the system, and then purge with stack gas before connecting to the previously evacuated bag.

8.2.1.3 Explosion Risk Area Bag Sampling Procedure. Follow 8.2.1.1 except replace the pump with another evacuated can (see Figure 18-9a). Use this method whenever there is a possibility of an explosion due to pumps, heated probes, or other flame producing equipment.

8.2.1.4 Other Modified Bag Sampling Procedures. In the event that condensation is observed in the bag while collecting the sample and a direct interface system cannot be used, heat the bag during collection, and maintain it at a suitably elevated temperature during all subsequent operations. (NOTE: Take care to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.) As an alternative, collect the sample gas, and simultaneously dilute it in the Tedlar bag.

8.2.1.4.1 First Alternative Procedure. Heat the box containing the sample bag to 120 °C (± 5 °C). Then transport the bag as rapidly as possible to the analytical area while maintaining the heating, or cover the box with an insulating blanket. In the analytical area, keep the box heated to 120 °C (±5 °C) until analysis. Be sure that the method of heating the box and the control for the heating circuit are compatible with the safety restrictions required in each area.

8.2.1.4.2 Second Alternative Procedure. Prefill the Tedlar bag with a known quantity of inert gas. Meter the inert gas into the bag according to the procedure for the preparation of gas concentration standards of volatile liquid materials (Section 10.1.2.2), but eliminate the midget impinger section. Take the partly filled bag to the source, and meter the source gas into the bag through heated sampling lines and a heated flowmeter, or Teflon positive displacement pump. Verify the dilution factors before sampling each bag through dilution and analysis of gases of known concentration.

8.2.1.5 Analysis of Bag Samples.

8.2.1.5.1 Apparatus. Same as Section 8.1. A minimum of three gas standards are required.

8.2.1.5.2 Procedure.

8.2.1.5.2.1 Establish proper GC operating conditions as described in Section 10.2, and record all data listed in Figure 18-7. Prepare the GC so that gas can be drawn through the sample valve. Flush the sample loop with calibration gas mixture, and activate the valve (sample pressure at the inlet to the GC introduction valve should be similar during calibration as during actual sample analysis). Obtain at least three chromatograms for the mixture. The results are acceptable when the peak areas for the three injections agree to within 5 percent of their average. If they do not agree, run additional samples or correct the analytical techniques until this requirement is met. Then analyze the other two calibration mixtures in the same manner. Prepare a calibration curve as described in Section 10.2.

8.2.1.5.2.2 Analyze the two field audit samples as described in Section 9.2 by connecting each Tedlar bag containing an audit gas mixture to the sampling valve. Calculate the results; record and report the data to the audit supervisor.

8.2.1.5.2.3 Analyze the three source gas samples by connecting each bag to the sampling valve with a piece of Teflon tubing identified with that bag. Analyze each bag sample three times. Record the data in Figure 18-11. If certain items do not apply, use the notation "N.A." If the

bag has been maintained at an elevated temperature as described in Section 8.2.1.4, determine the stack gas water content by Method 4. After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. Compare the average response factor of the pre- and post-test analysis for each compound. If they differ by > 5 percent, analyze the other calibration gas levels for that compound, and prepare a calibration curve using all the pre- and post-test calibration gas mixture values. If the two response factor averages (pre- and post-test) differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values.

8.2.1.6 Determination of Bag Water Vapor Content. Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.) If the bag has been maintained at an elevated temperature as described in Section 8.2.1.4, determine the stack gas water content by Method 4.

8.2.1.7 Audit Gas Analysis. Immediately prior to the analysis of the stack gas samples, perform audit analyses as described in Section 9.2.

8.2.1.8 Emission Calculations. From the calibration curve described in Section 8.2.1.5, select the value of C_s that corresponds to the peak area. Calculate the concentration C_c in ppm, dry basis, of each organic in the sample using Equation 18-5 in Section 12.6.

8.2.2 Direct Interface Sampling and Analysis Procedure. The direct interface procedure can be used provided that the moisture content of the gas does not interfere with the analysis procedure, the physical requirements of the equipment can be met at the site, and the source gas concentration falls within the linear range of the detector. Adhere to all safety requirements with this method.

8.2.2.1 Apparatus.

8.2.2.1.1 Probe. Constructed of stainless steel, Pyrex glass, or Teflon tubing as dictated by duct temperature and reactivity of target compounds. A filter or glass wool plug may be needed if particulate is present in the stack gas. If necessary, heat the probe with heating tape or a special heating unit capable of maintaining a temperature greater than 110°C.

8.2.2.1.2 Sample Lines. 6.4-mm OD (or other diameter as needed) Teflon lines, heat-traced to prevent condensation of material (greater than 110°C).

8.2.2.1.3 Quick Connects. To connect sample line to gas sampling valve on GC instrument and to pump unit used to withdraw source gas. Use a quick connect or equivalent on the cylinder or bag containing calibration gas to allow connection of the calibration gas to the gas sampling valve.

8.2.2.1.4 Thermocouple Readout Device. Potentiometer or digital thermometer, to measure source temperature and probe temperature.

8.2.2.1.5 Heated Gas Sampling Valve. Of two-position, six-port design, to allow sample loop to be purged with source gas or to direct source gas into the GC instrument.

8.2.2.1.6 Needle Valve. To control gas sampling rate from the source.

8.2.2.1.7 Pump. Leakless Teflon-coated diaphragm-type pump or equivalent, capable of at least 1 liter/minute sampling rate.

8.2.2.1.8 Flowmeter. Of suitable range to measure sampling rate.

8.2.2.1.9 Charcoal Adsorber. To adsorb organic vapor vented from the source to prevent exposure of personnel to source gas.

8.2.2.1.10 Gas Cylinders. Carrier gas, oxygen and fuel as needed to run GC and detector.

8.2.2.1.11 Gas Chromatograph. Capable of being moved into the field, with detector, heated gas sampling valve, column required to complete separation of desired components, and option for temperature programming.

8.2.2.1.12 Recorder/Integrator. To record results.

8.2.2.2 Procedure. Calibrate the GC using the procedures in Section 8.2.1.5.2.1. To obtain a stack gas sample, assemble the sampling system as shown in Figure 18-12. Make sure all connections are tight. Turn on the probe and sample line heaters. As the temperature of the probe and heated line approaches the target temperature as indicated on the thermocouple readout device, control the heating to maintain a temperature greater than 110°C. Conduct a 3-point calibration of the GC by analyzing each gas mixture in triplicate. Generate a calibration curve. Place the inlet of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and draw source gas into the probe, heated line, and sample loop. After thorough flushing, analyze the stack gas sample using the same conditions as for the calibration gas mixture. For each run, sample, analyze, and record five consecutive samples. A test consists of three runs (five samples per run times three runs, for a total of fifteen samples). After all samples have been analyzed, repeat the analysis of the mid-level calibration gas for each compound. For each

calibration standard, compare the pre- and post-test average response factors (RF) for each compound. If the two calibration RF values (pre and post-analysis) differ by more than 5 percent from their mean value, then analyze the other calibration gas levels for that compound and determine the stack gas sample concentrations by comparison to both calibration curves (this is done by preparing a calibration curve using all the pre and post-test calibration gas mixture values). If the two calibration RF values differ by less than 5 percent from their mean value, the tester has the option of using only the pre-test calibration curve to generate the concentration values. Record this calibration data and the other required data on the data sheet shown in Figure 18-11, deleting the dilution gas information.

(NOTE: Take care to draw all samples, calibration mixtures, and audits through the sample loop at the same pressure.)

8.2.2.3 Determination of Stack Gas Moisture Content. Use Method 4 to measure the stack gas moisture content.

8.2.2.4 Quality Assurance. Same as Section 8.2.1.7. Introduce the audit gases in the sample line immediately following the probe.

8.2.2.5 Emission Calculations. Same as Section 8.2.1.8.

8.2.3 Dilution Interface Sampling and Analysis Procedure. Source samples that contain a high concentration of organic materials may require dilution prior to analysis to prevent saturating the GC detector. The apparatus required for this direct interface procedure is basically the same as that described in the Section 8.2.2, except a dilution system is added between the heated sample line and the gas sampling valve. The apparatus is arranged so that either a 10:1 or 100:1 dilution of the source gas can be directed to the chromatograph. A pump of larger capacity is also required, and this pump must be heated and placed in the system between the sample line and the dilution apparatus.

8.2.3.1 Apparatus. The equipment required in addition to that specified for the direct interface system is as follows:

8.2.3.1.1 Sample Pump. Leakless Teflon-coated diaphragm-type that can withstand being heated to 120°C and deliver 1.5 liters/minute.

8.2.3.1.2 Dilution Pumps. Two Model A-150 Komhyr Teflon positive displacement type delivering 150 cc/minute, or equivalent. As an option, calibrated flowmeters can be used in conjunction with Teflon-coated diaphragm pumps.

8.2.3.1.3 Valves. Two Teflon three-way valves, suitable for connecting to Teflon tubing.

8.2.3.1.4 Flowmeters. Two, for measurement of diluent gas.

8.2.3.1.5 Diluent Gas with Cylinders and Regulators. Gas can be nitrogen or clean dry air, depending on the nature of the source gases.

8.2.3.1.6 Heated Box. Suitable for being heated to 120°C, to contain the three pumps, three-way valves, and associated connections. The box should be equipped with quick connect fittings to facilitate connection of: (1) the heated sample line from the probe, (2) the gas sampling valve, (3) the calibration gas mixtures, and (4) diluent gas lines. A schematic diagram of the components and connections is shown in Figure 18-13. The heated box shown in Figure 18-13 is designed to receive a heated line from the probe. An optional design is to build a probe unit that attaches directly to the heated box. In this way, the heated box contains the controls for the probe heaters, or, if the box is placed against the duct being sampled, it may be possible to eliminate the probe heaters. In either case, a heated Teflon line is used to connect the heated box to the gas sampling valve on the chromatograph.

NOTE: Care must be taken to leak-check the system prior to the dilutions so as not to create a potentially explosive atmosphere.

8.2.3.2 Procedure.

8.2.3.2.1 Assemble the apparatus by connecting the heated box, shown in Figure 18-13, between the heated sample line from the probe and the gas sampling valve on the chromatograph. Vent the source gas from the gas sampling valve directly to the charcoal filter, eliminating the pump and rotameter. Heat the sample probe, sample line, and heated box. Insert the probe and source thermocouple at the centroid of the duct, or to a point no closer to the walls than 1 m. Measure the source temperature, and adjust all heating units to a temperature 0 to 3°C above this temperature. If this temperature is above the safe operating temperature of the Teflon components, adjust the heating to maintain a temperature high enough to prevent condensation of water and organic compounds (greater than 110°C). Calibrate the GC through the dilution system by following the procedures in Section 8.2.1.5.2.1. Determine the concentration of the diluted calibration gas using the dilution factor and the certified concentration of the calibration gas. Record the pertinent data on the data sheet shown in Figure 18-11.

8.2.3.2.2 Once the dilution system and GC operations are satisfactory, proceed with the analysis of source gas, maintaining the same dilution settings as used for the standards.

8.2.3.2.3 Analyze the audit samples using either the dilution system, or directly connect to the gas sampling valve as required. Record all data and report the results to the audit supervisor.

8.2.3.3 Determination of Stack Gas Moisture Content. Same as Section 8.2.2.3.

8.2.3.4 Quality Assurance. Same as Section 8.2.2.4.

8.2.3.5 Emission Calculations. Same as section 8.2.2.5, with the dilution factor applied.

8.2.4 Adsorption Tube Procedure. Any commercially available adsorbent is allowed for the purposes of this method, as long as the recovery study criteria in Section 8.4.3 are met. Help in choosing the adsorbent may be found by calling the distributor, or the tester may refer to National Institute for Occupational Safety and Health (NIOSH) methods for the particular organics to be sampled. For some adsorbents, the principal interferent will be water vapor. If water vapor is thought to be a problem, the tester may place a midget impinger in an ice bath before the adsorbent tubes. If this option is chosen, the water catch in the midget impinger shall be analyzed for the target compounds. Also, the spike for the recovery study (in Section 8.4.3) shall be conducted in both the midget impinger and the adsorbent tubes. The combined recovery (add the recovered amount in the impinger and the adsorbent

tubes to calculate R) shall then meet the criteria in Section 8.4.3. **NOTE:** Post-test leak-checks are not allowed for this technique since this can result in sample contamination.

8.2.4.1 Additional Apparatus. The following items (or equivalent) are suggested.

8.2.4.1.1 Probe. Borosilicate glass or stainless steel, approximately 6-mm ID, with a heating system if water condensation is a problem, and a filter (either in-stack or out-of-stack, heated to stack temperature) to remove particulate matter. In most instances, a plug of glass wool is a satisfactory filter.

8.2.4.1.2 Flexible Tubing. To connect probe to adsorption tubes. Use a material that exhibits minimal sample adsorption.

8.2.4.1.3 Leakless Sample Pump. Flow controlled, constant rate pump, with a set of limiting (sonic) orifices.

8.2.4.1.4 Bubble-Tube Flowmeter. Volume accuracy within 1 percent, to calibrate pump.

8.2.4.1.5 Stopwatch. To time sampling and pump rate calibration.

8.2.4.1.6 Adsorption Tubes. Precleaned adsorbent, with mass of adsorbent to be determined by calculating breakthrough volume and expected concentration in the stack.

8.2.4.1.7 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure during sampling and pump calibration.

8.2.4.1.8 Rotameter. 0 to 100 cc/min, to detect changes in flow rate during sampling.

8.2.4.2 Sampling and Analysis.

8.2.4.2.1 Calibrate the pump and limiting orifice flow rate through adsorption tubes with the bubble tube flowmeter before sampling. The sample system can be operated as a "recirculating loop" for this operation. Record the ambient temperature and barometric pressure. Then, during sampling, use the rotameter to verify that the pump and orifice sampling rate remains constant.

8.2.4.2.2 Use a sample probe, if required, to obtain the sample at the centroid of the duct, or at a point no closer to the walls than 1 m. Minimize the length of flexible tubing between the probe and adsorption tubes. Several adsorption tubes can be connected in series, if the extra adsorptive capacity is needed. Adsorption tubes should be maintained vertically during the test in order to prevent channeling. Provide the gas sample to the sample system at a pressure sufficient for the limiting orifice to function as a sonic orifice. Record the total time and sample flow rate (or the number of pump strokes), the barometric pressure, and ambient temperature. Obtain a total sample volume commensurate with the expected

concentration(s) of the volatile organic(s) present, and recommended sample loading factors (weight sample per weight adsorption media). Laboratory tests prior to actual sampling may be necessary to predetermine this volume. If water vapor is present in the sample at concentrations above 2 to 3 percent, the adsorptive capacity may be severely reduced. Operate the gas chromatograph according to the manufacturer's instructions. After establishing optimum conditions, verify and document these conditions during all operations. Calibrate the instrument. Analyze the audit samples (see Section 16.1.4.3), then the emission samples.

8.2.4.3 Standards and Calibration. If using thermal desorption, obtain calibration gases using the procedures in Section 10.1. If using solvent extraction, prepare liquid standards in the desorption solvent. Use a minimum of three different standards; select the concentrations to bracket the expected average sample concentration. Perform the calibration before and after each day's sample analyses using the procedures in Section 8.2.1.5.2.1.

8.2.4.4 Quality Assurance.

8.2.4.4.1 Determine the recovery efficiency of the pollutants of interest according to Section 8.4.3.

8.2.4.4.2 Determination of Sample Collection Efficiency (Optional). If sample breakthrough is thought to be a problem, a routine procedure for determining

breakthrough is to analyze the primary and backup portions of the adsorption tubes separately. If the backup portion exceeds 10 percent of the total amount (primary and back-up), it is usually a sign of sample breakthrough. For the purposes of this method, only the recovery efficiency value (Section 8.4.3) is used to determine the appropriateness of the sampling and analytical procedure.

8.2.4.4.3 Volume Flow Rate Checks. Perform this check immediately after sampling with all sampling train components in place. Use the bubble-tube flowmeter to measure the pump volume flow rate with the orifice used in the test sampling, and record the result. If it has changed by more than 5 but less than 20 percent, calculate an average flow rate for the test. If the flow rate has changed by more than 20 percent, recalibrate the pump and repeat the sampling.

8.2.4.4.4 Calculations. Correct all sample volumes to standard conditions. If a sample dilution system has been used, multiply the results by the appropriate dilution ratio. Correct all results according to the applicable procedure in Section 8.4.3. Report results as ppm by volume, dry basis.

8.3 Reporting of Results. At the completion of the field analysis portion of the study, ensure that the data

sheets shown in Figure 18-11 have been completed. Summarize this data on the data sheets shown in Figure 18-15.

8.4 Recovery Study. After conducting the presurvey and identifying all of the pollutants of interest, conduct the appropriate recovery study during the test based on the sampling system chosen for the compounds of interest.

8.4.1 Recovery Study for Direct Interface or Dilution Interface Sampling. If the procedures in Section 8.2.2 or 8.2.3 are to be used to analyze the stack gas, conduct the calibration procedure as stated in Section 8.2.2.2 or 8.2.3.2, as appropriate. Upon successful completion of the appropriate calibration procedure, attach the mid-level calibration gas for at least one target compound to the inlet of the probe or as close as possible to the inlet of the probe, but before the filter. Repeat the calibration procedure by sampling and analyzing the mid-level calibration gas through the entire sampling and analytical system in triplicate. The mean of the calibration gas response sampled through the probe shall be within 10 percent of the analyzer response. If the difference in the two means is greater than 10 percent, check for leaks throughout the sampling system and repeat the analysis of the standard through the sampling system until this criterion is met.

8.4.2 Recovery Study for Bag Sampling.

8.4.2.1 Follow the procedures for the bag sampling and analysis in Section 8.2.1. After analyzing all three bag samples, choose one of the bag samples and tag this bag as the spiked bag. Spike the chosen bag sample with a known mixture (gaseous or liquid) of all of the target pollutants. The theoretical concentration, in ppm, of each spiked compound in the bag shall be 40 to 60 percent of the average concentration measured in the three bag samples. If a target compound was not detected in the bag samples, the concentration of that compound to be spiked shall be 5 times the limit of detection for that compound. Store the spiked bag for the same period of time as the bag samples collected in the field. After the appropriate storage time has passed, analyze the spiked bag three times. Calculate the average fraction recovered (R) of each spiked target compound with the equation in Section 12.7.

8.4.2.2 For the bag sampling technique to be considered valid for a compound, $0.70 \leq R \leq 1.30$. If the R value does not meet this criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R

value for that compound by using the equation in Section 12.8.

8.4.3 Recovery Study for Adsorption Tube Sampling. If following the adsorption tube procedure in Section 8.2.4, conduct a recovery study of the compounds of interest during the actual field test. Set up two identical sampling trains. Collocate the two sampling probes in the stack. The probes shall be placed in the same horizontal plane, where the first probe tip is 2.5 cm from the outside edge of the other. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike all of the compounds of interest (in gaseous or liquid form) onto the adsorbent tube(s) in the spiked train before sampling. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be collected with the unspiked train. Sample the stack gas into the two trains simultaneously. Analyze the adsorbents from the two trains utilizing identical analytical procedures and instrumentation. Determine the fraction of spiked compound recovered (R) using the equations in Section 12.9.

8.4.3.1 Repeat the procedure in Section 8.4.3 twice more, for a total of three runs. In order for the adsorbent tube sampling and analytical procedure to be acceptable for a compound, $0.70 \leq R \leq 1.30$ (R in this case is the average of three runs). If the average R value does not meet this

criterion for a target compound, the sampling technique is not acceptable for that compound, and therefore another sampling technique shall be evaluated for acceptance (by repeating the recovery study with another sampling technique). Report the R value in the test report and correct all field measurements with the calculated R value for that compound by using the equation in Section 12.8.

9.0 Quality Control.

9.1 Miscellaneous Quality Control Measures

Section	Quality Control Measure	Effect
8.4.1	Recovery study for direct interface or dilution interface sampling.	Ensure that there are no significant leaks in the sampling system.
8.4.2	Recovery study for bag sampling.	Demonstrate that proper sampling/analysis procedures were selected.
8.4.3	Recovery study for adsorption tube sampling.	Demonstrate that proper sampling/analysis procedures were selected.

9.2 Quality Assurance for Laboratory Procedures. Immediately after the preparation of the calibration curves, the analysis audit described in 40 CFR Part 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis," should be performed if audit materials are available. The information required to document the analysis of the audit samples has been included on the example data sheets shown in Figures 18-3 and 18-7. The audit analyses should agree

with the certified audit concentrations within 10 percent. Audit sample results shall be submitted according to directions provided with the audit samples.

10.0 Calibration and Standardization.

10.1 Calibration Standards. Obtain calibration gas standards for each target compound to be analyzed. Commercial cylinder gases certified by the manufacturer to be accurate to within 1 percent of the certified label value are preferable, although cylinder gases certified by the manufacturer to 2 percent accuracy are allowed. Another option allowed by this method is for the tester to obtain high concentration certified cylinder gases and then use a dilution system meeting the requirements of Test Method 205, 40 CFR Part 51, Appendix M to make multi-level calibration gas standards. Prepare or obtain enough calibration standards so that there are three different concentrations of each organic compound expected to be measured in the source sample. For each organic compound, select those concentrations that bracket the concentrations expected in the source samples. A calibration standard may contain more than one organic compound. If samples are collected in adsorbent tubes and extracted using solvent extraction, prepare or obtain standards in the same solvent used for the

sample extraction procedure. Verify the stability of all standards for the time periods they are used.

10.2 Preparation of Calibration Curves.

10.2.1 Establish proper GC conditions, then flush the sampling loop for 30 seconds. Allow the sample loop pressure to equilibrate to atmospheric pressure, and activate the injection valve. Record the standard concentration, attenuator factor, injection time, chart speed, retention time, peak area, sample loop temperature, column temperature, and carrier gas flow rate. Analyze each standard in triplicate.

10.2.2 Repeat this procedure for each standard. Prepare a graphical plot of concentration (C_s) versus the calibration area values. Perform a regression analysis, and draw the least square line.

11.0 Analytical Procedures.

11.1 Analysis Development.

11.1.1 Selection of GC Parameters.

11.1.1.1 Column Choice. Based on the initial contact with plant personnel concerning the plant process and the anticipated emissions, choose a column that provides good resolution and rapid analysis time. The choice of an appropriate column can be aided by a literature search,

contact with manufacturers of GC columns, and discussion with personnel at the emission source.

NOTE: Most column manufacturers keep excellent records on their products. Their technical service departments may be able to recommend appropriate columns and detector type for separating the anticipated compounds, and they may be able to provide information on interferences, optimum operating conditions, and column limitations. Plants with analytical laboratories may be able to provide information on their analytical procedures.

11.1.1.2 Preliminary GC Adjustment. Using the standards and column obtained in Section 11.1.1.1, perform initial tests to determine appropriate GC conditions that provide good resolution and minimum analysis time for the compounds of interest.

11.1.1.3 Preparation of Presurvey Samples. If the samples were collected on an adsorbent, extract the sample as recommended by the manufacturer for removal of the compounds with a solvent suitable to the type of GC analysis. Prepare other samples in an appropriate manner.

11.1.1.4 Presurvey Sample Analysis.

11.1.1.4.1 Before analysis, heat the presurvey sample to the duct temperature to vaporize any condensed material. Analyze the samples by the GC procedure, and compare the

retention times against those of the calibration samples that contain the components expected to be in the stream. If any compounds cannot be identified with certainty by this procedure, identify them by other means such as GC/mass spectroscopy (GC/MS) or GC/infrared techniques. A GC/MS system is recommended.

11.1.1.4.2 Use the GC conditions determined by the procedure of Section 11.1.1.2 for the first injection. Vary the GC parameters during subsequent injections to determine the optimum settings. Once the optimum settings have been determined, perform repeat injections of the sample to determine the retention time of each compound. To inject a sample, draw sample through the loop at a constant rate (100 ml/min for 30 seconds). Be careful not to pressurize the gas in the loop. Turn off the pump and allow the gas in the sample loop to come to ambient pressure. Activate the sample valve, and record injection time, loop temperature, column temperature, carrier flow rate, chart speed, and attenuator setting. Calculate the retention time of each peak using the distance from injection to the peak maximum divided by the chart speed. Retention times should be repeatable within 0.5 seconds.

11.1.1.4.3 If the concentrations are too high for appropriate detector response, a smaller sample loop or dilutions may be used for gas samples, and, for liquid

samples, dilution with solvent is appropriate. Use the standard curves (Section 10.2) to obtain an estimate of the concentrations.

11.1.1.4.4 Identify all peaks by comparing the known retention times of compounds expected to be in the retention times of peaks in the sample. Identify any remaining unidentified peaks which have areas larger than 5 percent of the total using a GC/MS, or estimation of possible compounds by their retention times compared to known compounds, with confirmation by further GC analysis.

12.0 Data Analysis and Calculations.

12.1 Nomenclature.

B_{ws} = Water vapor content of the bag sample or stack gas, proportion by volume.

C_s = Concentration of the organic from the calibration curve, ppm.

G_v = Gas volume or organic compound injected, ml.

L_v = Liquid volume of organic injected, μl.

M = Molecular weight of organic, g/g-mole.

m_s = Total mass of compound measured on adsorbent with spiked train (μg).

m_u = Total mass of compound measured on adsorbent with unspiked train (μg).

m_v = Mass per volume of spiked compound measured (μg/L).

P_i = Barometric or absolute sample loop pressure at time of sample analysis, mm Hg.

P_m = Absolute pressure of dry gas meter, mm Hg.

P_r = Reference pressure, the barometric pressure or absolute sample loop pressure recorded during calibration, mm Hg.

P_s = Absolute pressure of syringe before injection, mm Hg.

q_c = Flow rate of the calibration gas to be diluted.

q_{c1} = Flow rate of the calibration gas to be diluted in stage 1.

q_{c2} = Flow rate of the calibration gas to be diluted in stage 2.

q_d = Diluent gas flow rate.

q_{d1} = Flow rate of diluent gas in stage 1.

q_{d2} = Flow rate of diluent gas in stage 2.

s = Theoretical concentration (ppm) of spiked target compound in the bag.

S = Theoretical mass of compound spiked onto adsorbent in spiked train (μg).

t = Measured average concentration (ppm) of target compound and source sample (analysis results subsequent to bag spiking)

T_i = Sample loop temperature at the time of sample analysis, °K.

T_m = Absolute temperature of dry gas meter, °K.

T_s = Absolute temperature of syringe before injection, °K.

u = Source sample average concentration (ppm) of target compound in the bag (analysis results before bag spiking).

V_m = Gas volume indicated by dry gas meter, liters.

v_s = volume of stack gas sampled with spiked train (L).

v_u = volume of stack gas sampled with unspiked train (L).

X = Mole or volume fraction of the organic in the calibration gas to be diluted.

Y = Dry gas meter calibration factor, dimensionless.

μl = Liquid organic density as determined, g/ml.

24.055 = Ideal gas molar volume at 293 °K and 760 mm Hg, liters/g-mole.

1000 = Conversion factor, ml/liter.

10^6 = Conversion to ppm.

12.2 Calculate the concentration, C_s, in ppm using the following equation:

$$C_s = \frac{10^6 \ (\overline{X} \ q_c)}{q_c + q_d} \qquad \textbf{Eq. 18-1}$$

12.3 Calculate the concentration, C_s, in ppm of the organic in the final gas mixture using the following equation:

$$C_s = 10^6 \overline{X} \left(\frac{q_{c1}}{q_{c1} + q_{d1}} \right) \left(\frac{q_{c2}}{q_{c2} + q_{d2}} \right) \qquad \textbf{Eq. 18-2}$$

12.4 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{G_v \times 10^6 \ \frac{293}{T_s} \frac{P_s}{760}}{V_m \ Y \ \frac{293}{T_m} \ \frac{P_m}{760} \ 1000} \qquad \textbf{Eq. 18-3}$$

$$= \frac{G_v \times 10^3 \ \frac{P_s}{T_s} \ \frac{T_m}{P_m}}{V_m \ Y}$$

12.5 Calculate each organic standard concentration, C_s, in ppm using the following equation:

$$C_s = \frac{\frac{L_v}{M} \bullet (24.055 \times 10^6)}{V_m Y \frac{293}{T_m} \frac{P_m}{760} 1000} = 6.24 \times 10^4 \frac{L_v \bullet T_m}{M V_m Y P_m} \qquad \textbf{Eq. 18-4}$$

12.6 Calculate the concentration, C_c, in ppm, dry basis, of each organic is the sample using the following equation:

$$C_C = \frac{C_s P_r T_i F_r}{P_i T_r (1-B_{ws})} \qquad \textbf{Eq. 18-5}$$

12.7 Calculate the average fraction recovered (R) of each spiked target compound using the following equation:

$$R = \frac{t-u}{s} \qquad \textbf{Eq. 18-6}$$

12.8 Correct all field measurements with the calculated R value for that compound using the following equation:

$$\text{Reported Result} = \frac{\text{Measured Concentration (ppm)}}{R} \qquad \textbf{Eq. 18-7}$$

12.9 Determine the mass per volume of spiked compound measured using the following equation:

$$m_v = \frac{m_s}{v_s} - \frac{m_u}{v_u} \qquad \textbf{Eq. 18-8}$$

12.10 Calculate the fraction of spiked compound recovered, R, using the following equation:

$$R = \frac{m_v \times v_s}{S} \qquad \textbf{Eq. 18-9}$$

13.0 Method Performance.

13.1 Since a potential sample may contain a variety of compounds from various sources, a specific precision limit for the analysis of field samples is impractical. Precision in the range of 5 to 10 percent relative standard deviation (RSD) is typical for gas chromatographic techniques, but an experienced GC operator with a reliable instrument can readily achieve 5 percent RSD. For this method, the following combined GC/operator values are required.

(a) Precision. Triplicate analyses of calibration standards fall within 5 percent of their mean value.

(b) Accuracy. Analysis results of prepared audit samples are within 10 percent of preparation values.

(c) Recovery. After developing an appropriate sampling and analytical system for the pollutants of interest, conduct the procedure in Section 8.4. Conduct the appropriate recovery study in Section 8.4 at each sampling point where the method is being applied. Submit the data and results of the recovery procedure with the reporting of results under Section 8.3.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures.

16.1 Optional Presurvey and Presurvey Sampling.

NOTE: Presurvey screening is optional. Presurvey sampling should be conducted for sources where the target pollutants are not known from previous tests and/or process knowledge.

Perform a presurvey for each source to be tested. Refer to Figure 18-1. Some of the information can be collected from literature surveys and source personnel. Collect gas samples that can be analyzed to confirm the identities and approximate concentrations of the organic emissions.

16.1.1 Apparatus. This apparatus list also applies to Sections 8.2 and 11.

16.1.1.1 Teflon Tubing. (Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.) Diameter and length determined by connection requirements of cylinder regulators and the GC. Additional tubing is necessary to connect the GC sample loop to the sample.

16.1.1.2 Gas Chromatograph. GC with suitable detector, columns, temperature-controlled sample loop and valve assembly, and temperature programmable oven, if necessary. The GC shall achieve sensitivity requirements for the compounds under study.

16.1.1.3 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

16.1.1.4 Flow Meter. To measure flow rates.

16.1.1.5 Regulators. Used on gas cylinders for GC and for cylinder standards.

16.1.1.6 Recorder. Recorder with linear strip chart is minimum acceptable. Integrator (optional) is recommended.

16.1.1.7 Syringes. 0.5-ml, 1.0- and 10-microliter size, calibrated, maximum accuracy (gas tight) for preparing calibration standards. Other appropriate sizes can be used.

16.1.1.8 Tubing Fittings. To plumb GC and gas cylinders.

16.1.1.9 Septa. For syringe injections.

16.1.1.10 Glass Jars. If necessary, clean, colored glass jars with Teflon-lined lids for condensate sample collection. Size depends on volume of condensate.

16.1.1.11 Soap Film Flowmeter. To determine flow rates.

16.1.1.12 Tedlar Bags. 10- and 50-liter capacity, for preparation of standards.

16.1.1.13 Dry Gas Meter with Temperature and Pressure Gauges. Accurate to ± 2 percent, for preparation of gas standards.

16.1.1.14 Midget Impinger/Hot Plate Assembly. For preparation of gas standards.

16.1.1.15 Sample Flasks. For presurvey samples, must have gas-tight seals.

16.1.1.16 Adsorption Tubes. If necessary, blank tubes filled with necessary adsorbent (charcoal, Tenax, XAD-2, etc.) for presurvey samples.

16.1.1.17 Personnel Sampling Pump. Calibrated, for collecting adsorbent tube presurvey samples.

16.1.1.18 Dilution System. Calibrated, the dilution system is to be constructed following the specifications of an acceptable method.

16.1.1.19 Sample Probes. Pyrex or stainless steel, of sufficient length to reach centroid of stack, or a point no closer to the walls than 1 m.

16.1.1.20 Barometer. To measure barometric pressure.

16.1.2 Reagents.

16.1.2.1 Water. Deionized distilled.

16.1.2.2 Methylene chloride.

16.1.2.3 Calibration Gases. A series of standards prepared for every compound of interest.

16.1.2.4 Organic Compound Solutions. Pure (99.9 percent), or as pure as can reasonably be obtained, liquid samples of all the organic compounds needed to prepare calibration standards.

16.1.2.5 Extraction Solvents. For extraction of adsorbent tube samples in preparation for analysis.

16.1.2.6 Fuel. As recommended by the manufacturer for operation of the GC.

16.1.2.7 Carrier Gas. Hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column.

16.1.2.8 Zero Gas. Hydrocarbon free air or nitrogen, to be used for dilutions, blank preparation, and standard preparation.

16.1.3 Sampling.

16.1.3.1 Collection of Samples with Glass Sampling Flasks. Presurvey samples may be collected in precleaned 250-ml double-ended glass sampling flasks. Teflon stopcocks, without grease, are preferred. Flasks should be cleaned as follows: Remove the stopcocks from both ends of the flasks, and wipe the parts to remove any grease. Clean the stopcocks, barrels, and receivers with methylene chloride (or other non-target pollutant solvent, or heat and humidified air). Clean all glass ports with a soap solution, then rinse with tap and deionized distilled water. Place the flask in a cool glass annealing furnace, and apply heat up to 500°C. Maintain at this temperature for 1 hours. After this time period, shut off and open the furnace to allow the flask to cool. Return the stopcocks to the flask receivers. Purge the assembly with high-purity nitrogen for 2 to 5 minutes. Close off the stopcocks after purging to

maintain a slight positive nitrogen pressure. Secure the stopcocks with tape. Presurvey samples can be obtained either by drawing the gases into the previously evacuated flask or by drawing the gases into and purging the flask with a rubber suction bulb.

16.1.3.1.1 Evacuated Flask Procedure. Use a high-vacuum pump to evacuate the flask to the capacity of the pump; then close off the stopcock leading to the pump. Attach a 6-mm outside diameter (OD) glass tee to the flask inlet with a short piece of Teflon tubing. Select a 6-mm OD borosilicate sampling probe, enlarged at one end to a 12-mm OD and of sufficient length to reach the centroid of the duct to be sampled. Insert a glass wool plug in the enlarged end of the probe to remove particulate matter. Attach the other end of the probe to the tee with a short piece of Teflon tubing. Connect a rubber suction bulb to the third leg of the tee. Place the filter end of the probe at the centroid of the duct, and purge the probe with the rubber suction bulb. After the probe is completely purged and filled with duct gases, open the stopcock to the grab flask until the pressure in the flask reaches duct pressure. Close off the stopcock, and remove the probe from the duct. Remove the tee from the flask and tape the stopcocks to prevent leaks during shipment. Measure and record the duct temperature and pressure.

16.1.3.1.2 Purged Flask Procedure. Attach one end of the sampling flask to a rubber suction bulb. Attach the other end to a 6-mm OD glass probe as described in Section 8.3.3.1.1. Place the filter end of the probe at the centroid of the duct, or at a point no closer to the walls than 1 m, and apply suction with the bulb to completely purge the probe and flask. After the flask has been purged, close off the stopcock near the suction bulb, and then close off the stopcock near the probe. Remove the probe from the duct, and disconnect both the probe and suction bulb. Tape the stopcocks to prevent leakage during shipment. Measure and record the duct temperature and pressure.

16.1.3.2 Flexible Bag Procedure. Tedlar or aluminized Mylar bags can also be used to obtain the presurvey sample. Use new bags, and leak-check them before field use. In addition, check the bag before use for contamination by filling it with nitrogen or air, and analyzing the gas by GC at high sensitivity. Experience indicates that it is desirable to allow the inert gas to remain in the bag about 24 hours or longer to check for desorption of organics from the bag. Follow the leak-check and sample collection procedures given in Section 8.2.1.

16.1.3.3 Determination of Moisture Content. For combustion or water- controlled processes, obtain the moisture content from plant personnel or by measurement

during the presurvey. If the source is below 59°C, measure the wet bulb and dry bulb temperatures, and calculate the moisture content using a psychrometric chart. At higher temperatures, use Method 4 to determine the moisture content.

16.1.4 Determination of Static Pressure. Obtain the static pressure from the plant personnel or measurement. If a type S pitot tube and an inclined manometer are used, take care to align the pitot tube 90° from the direction of the flow. Disconnect one of the tubes to the manometer, and read the static pressure; note whether the reading is positive or negative.

16.1.5 Collection of Presurvey Samples with Adsorption Tube. Follow Section 8.2.4 for presurvey sampling.

17.0 References.

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18.0 Tables, Diagrams, Flowcharts, and Validation Data.

I. Name of company_____ Date_____
Address _____
_____
Contacts _____ Phone_____
Process to be sampled_____
_____

_____

Duct or vent to be sampled _____
_____
II. Process description _____
_____
_____
_____
_____
Raw material _____
_____
_____
Products _____
_____
_____

Operating cycle
Check: Batch _____ Continuous _____ Cyclic _____
Timing of batch or cycle _____
Best time to test _____

Figure 18-1. Preliminary survey data sheet.

III. Sampling site

A. Description

Site description _____

Duct shape and size _____

Material _____

Wall thickness _____ inches

Upstream distance _____ inches _____ diameter

Downstream distance _____ inches _____ diameter

Size of port _____

Size of access area _____

Hazards _____ Ambient temp. _____ °F

B. Properties of gas stream

Temperature _____ °C _____ °F, Date source _____

Velocity _____, Data source _____

Static pressure _____ inches H_2O, Data source _____

Moisture content _____ %, Data source _____

Particulate content _____, Data source _____

Gaseous components

N_2	_____ %	Hydrocarbons	_____ ppm
O_2	_____ %	_____	_____
CO	_____ %	_____	_____
CO_2	_____ %	_____	_____
SO_2	_____ %	_____	_____

Hydrocarbon components

_____	_____	ppm
_____	_____	ppm
_____	_____	ppm
_____	_____	ppm
_____	_____	ppm
_____	_____	ppm

Figure 18-1 (continued). Preliminary survey data sheet.

C. Sampling considerations

Location to set up GC _____

_____

Special hazards to be considered _____

_____

Power available at duct _____

Power available for GC _____

Plant safety requirements _____

_____

Vehicle traffic rules _____

_____

Plant entry requirements _____

_____

Security agreements _____

_____

Potential problems _____

_____

D. Site diagrams. (Attach additional sheets if required).

Figure 18-1 (continued). Preliminary survey data sheet.

Components_to_be_analyzed	Expected_concentration
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____
_____	_____

Suggested chromatographic column _____

_____

Column flow rate _____ ml/min Head pressure _____ mm Hg

Column temperature:

Isothermal _____ °C

Programmed from _____ °C to _____ °C at _____ °C/min

Injection port/sample loop temperature _____ °C

Detector temperature _____ °C

Detector flow rates: Hydrogen _____ ml/min.

head pressure _____ mm Hg

Air/Oxygen _____ ml/min.

head pressure _____ mm Hg

Chart speed _____ inches/minute

Compound data:

Compound	Retention_time	Attenuation
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Figure 18-2. Chromatographic conditions data sheet.

Figure 18-3. Preparation of Standards in Tedlar Bags and Calibration Curve.

	Standards		
Standards Preparation Data:	Mixture #1	Mixture #2	Mixture #3
Organic:			
Bag number or identification			
Dry gas meter calibration factor			
Final meter reading (liters)			
Initial meter reading (liters)			
Metered volume (liters)			
Average meter temperature (°K)			
Average meter pressure, gauge (mm Hg)			
Average atmospheric pressure (mm Hg)			
Average meter pressure, absolute (mm Hg)			
Syringe temperature (°K) (see Section 10.1.2.1)			
Syringe pressure, absolute (mm Hg) (see Section 10.1.2.1)			
Volume of gas in syringe (ml) (Section 10.1.2.1)			
Density of liquid organic (g/ml) (Section 10.1.2.2)			
Volume of liquid in syringe (ml) (Section 10.1.2.2)			
GC Operating Conditions:			
Sample loop volume (ml)			
Sample loop temperature (°C)			

Carrier gas flow rate (ml/min)			
Column temperature			
Initial (°C)			
Rate change (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24 hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Organic retention time (min)			
Attenuation factor			
Peak height (mm)			
Peak area (mm_2)			
Peak area * attenuation factor (mm_2)			
Calculated concentration (ppm) (Equation 18-3 or 18-4)			
Plot peak area * attenuation factor against calculated concentration to obtain calibration curve.			

Figure 18-3 (continued). Standards prepared in Tedlar bags and calibration curve.

Figure 18-4. Flowmeter Calibration.

Flowmeter number or identification _____
Flowmeter Type _____
Method: Bubble meter _____ Spirometer _____ Wet test meter _____
Readings at laboratory conditions:
Laboratory temperature (T_{lab}) _____ °K
Laboratory barometric pressure (P_{lab}) _____ mm Hg
Flow data:

Flowmeter		
reading (as marked)	temp. (°K)	pressure (absolute)

Calibration device		
Time (min)	Gas Volume[a]	Flow Rate[b]

[a]Vol. of gas may be measured in milliliters, liters or cubic feet.

[b]Convert to standard conditions (20°C and 760 mm Hg).

Plot flowmeter reading against flow rate (standard conditions), and draw a smooth curve. If the flowmeter being calibrated is a rotameter or other flow device that is viscosity dependent, it may be necessary to generate a "family" of calibration curves that cover the operating pressure and temperature ranges of the flowmeter.

While the following technique should be verified before application, it may be possible to calculate flow rate reading for rotameters at standard conditions Q_{std} as follows:

$$Q_{std} = Q_{lab}\left(\frac{760 \times T_{lab}}{P_{lab} \times 293}\right)^{1/2}$$

Flow rate (laboratory conditions)	Flow rate (STD_conditions)

Figure 18-4 (continued). Flowmeter calibration.

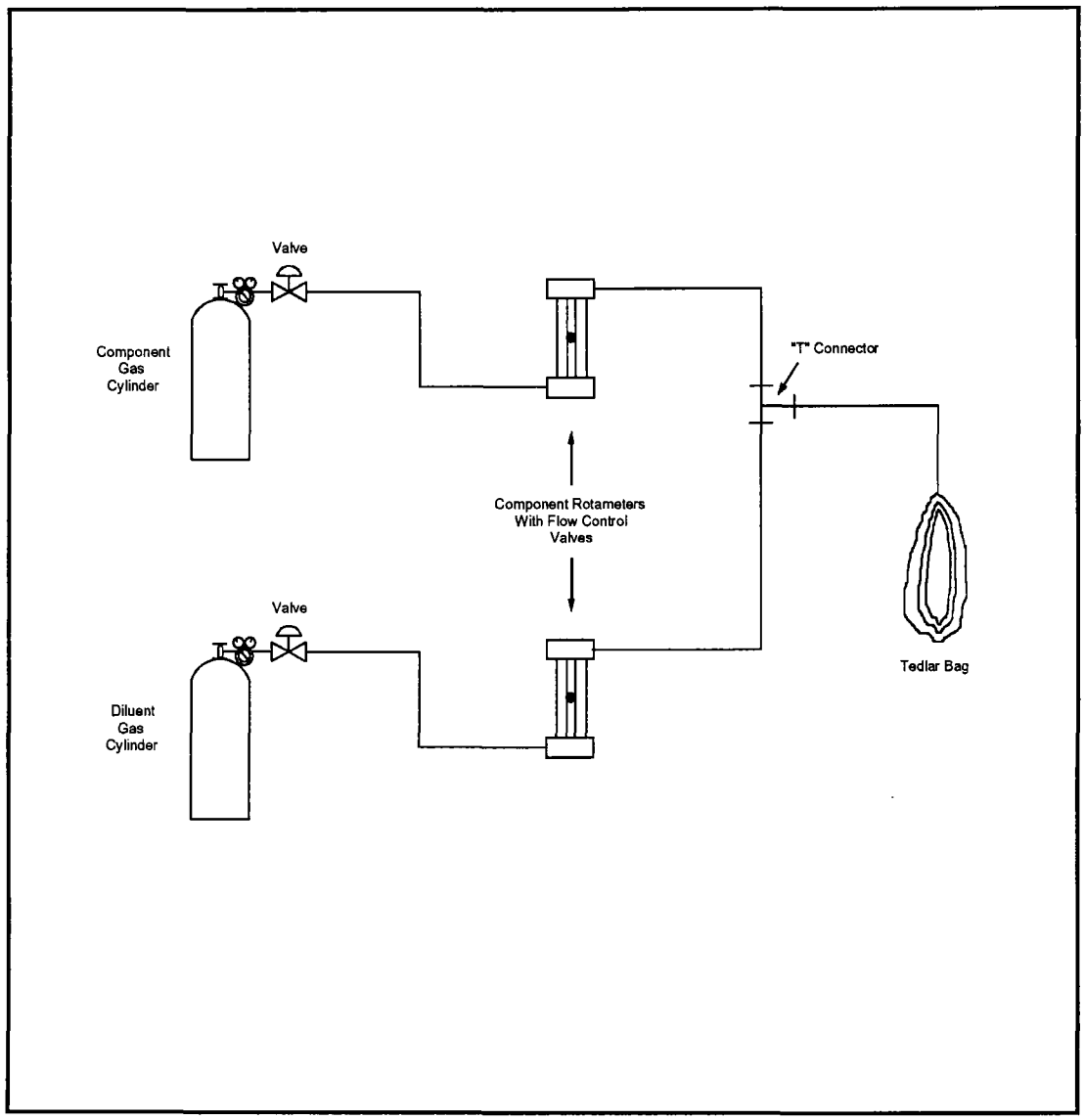

Figure 18-5. Single-Stage Calibration Gas Dilution System.

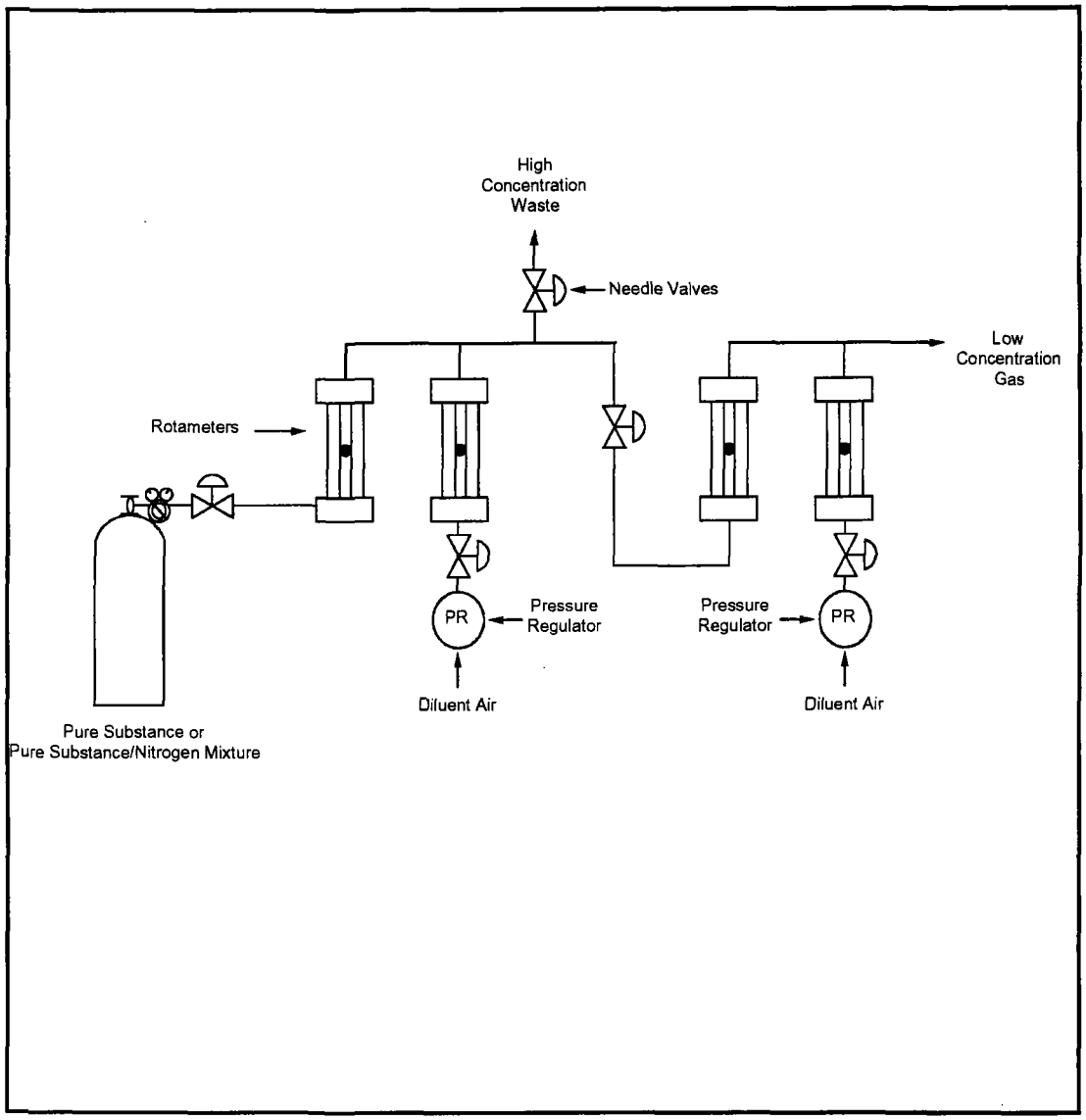

Figure 18-6. Two-Stage Dilution Apparatus.

Preparation of Standards by Dilution of Cylinder Standard

Cylinder Standard: Organic _____ Certified Concentration ____ ppm			
Standards Preparation Data:	Date:		
Stage 1	Mixture 1	Mixture 2	Mixture 3
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Laboratory temperature (°K)			
Barometric pressure (mm Hg)			
Flowmeter gage pressure (mm Hg)			
Flow rate cylinder gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions (ml/min)			
Calculated concentration (ppm)			
Stage 2 (if used)			
Standard gas flowmeter reading			
Diluent gas flowmeter reading			
Flow rate Stage 1 gas at standard conditions (ml/min)			
Flow rate diluent gas at standard conditions			
Calculated concentration (ppm)			
GC Operating Conditions:			
Sample loop volume (ml)			

Sample loop temperature (°C)			
Carrier gas flow rate (ml/min)			
Column temperature:			
Initial (°C)			
Program rate (°C/min)			
Final (°C)			
Organic Peak Identification and Calculated Concentrations:			
Injection time (24-hour clock)			
Distance to peak (cm)			
Chart speed (cm/min)			
Retention time (min)			
Attenuation factor			
Peak area (mm^2)			
Peak area * attenuation factor			
Plot peak area * attenuation factor against calculated concentration to obtain calibration curve.			

Figure 18-7. Standards prepared by dilution of cylinder standard.

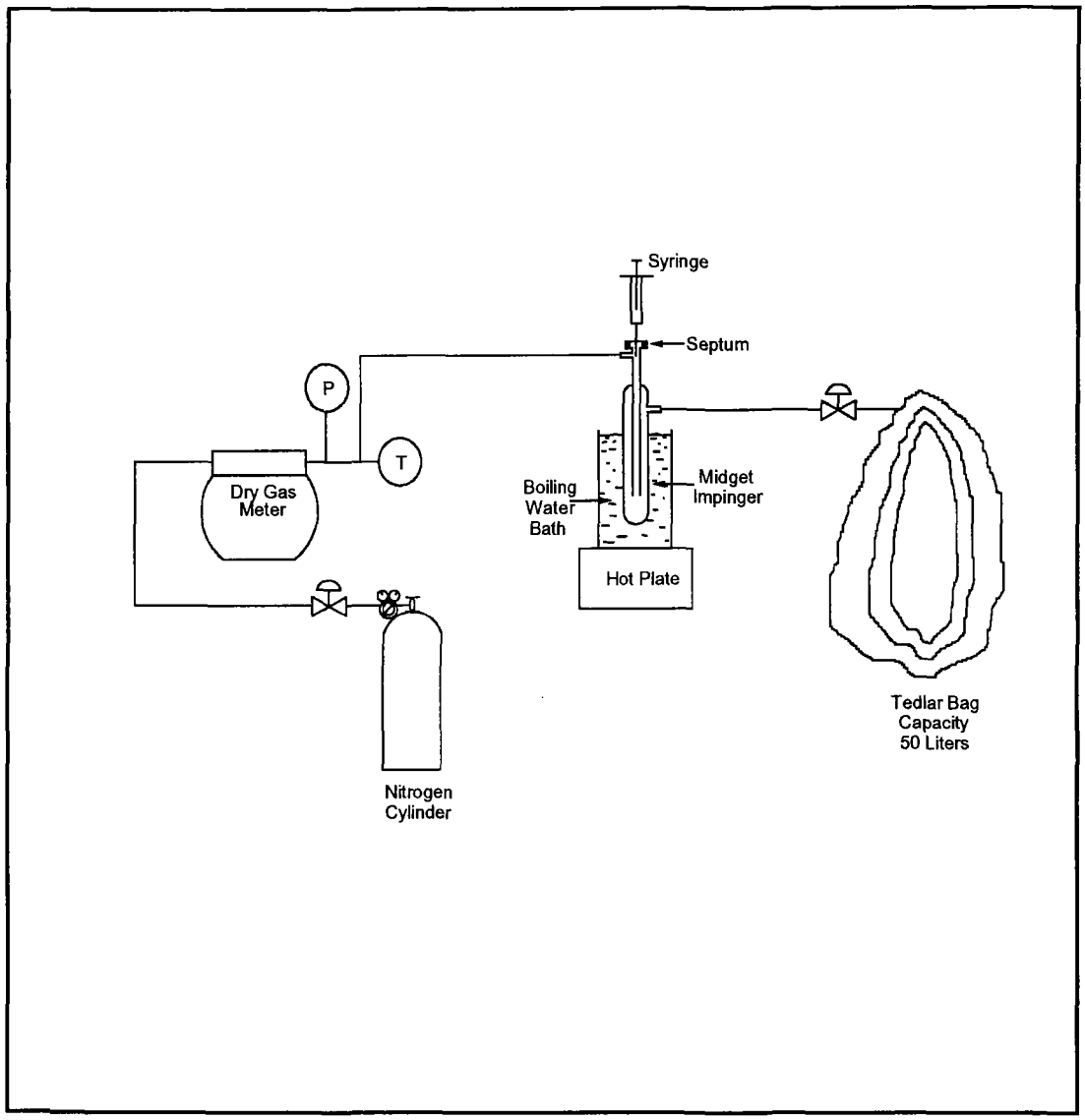

Figure 18-8. Apparatus for Preparation of Liquid Materials.

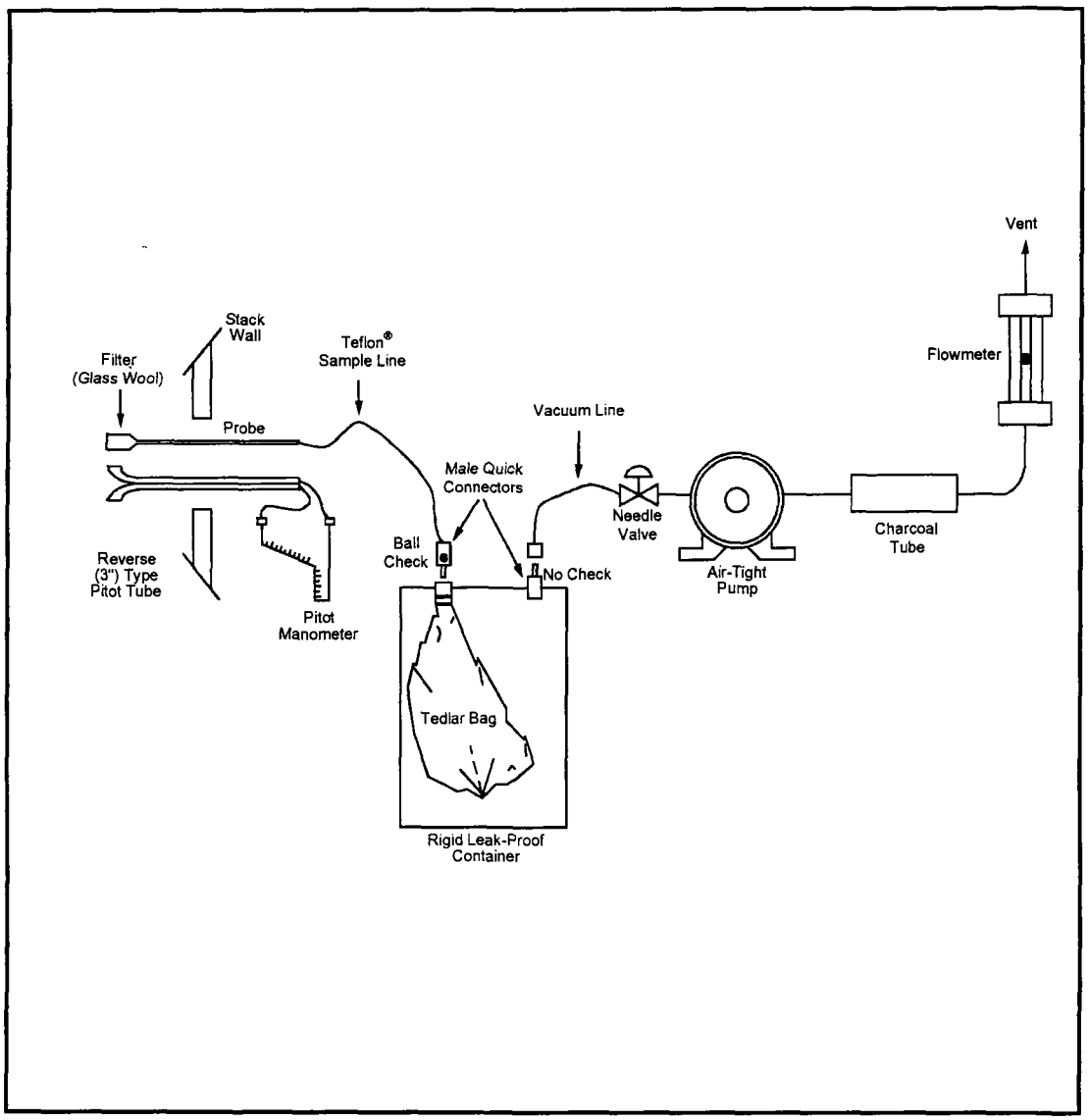

Figure 18-9. Integrated Bag Sampling Train.

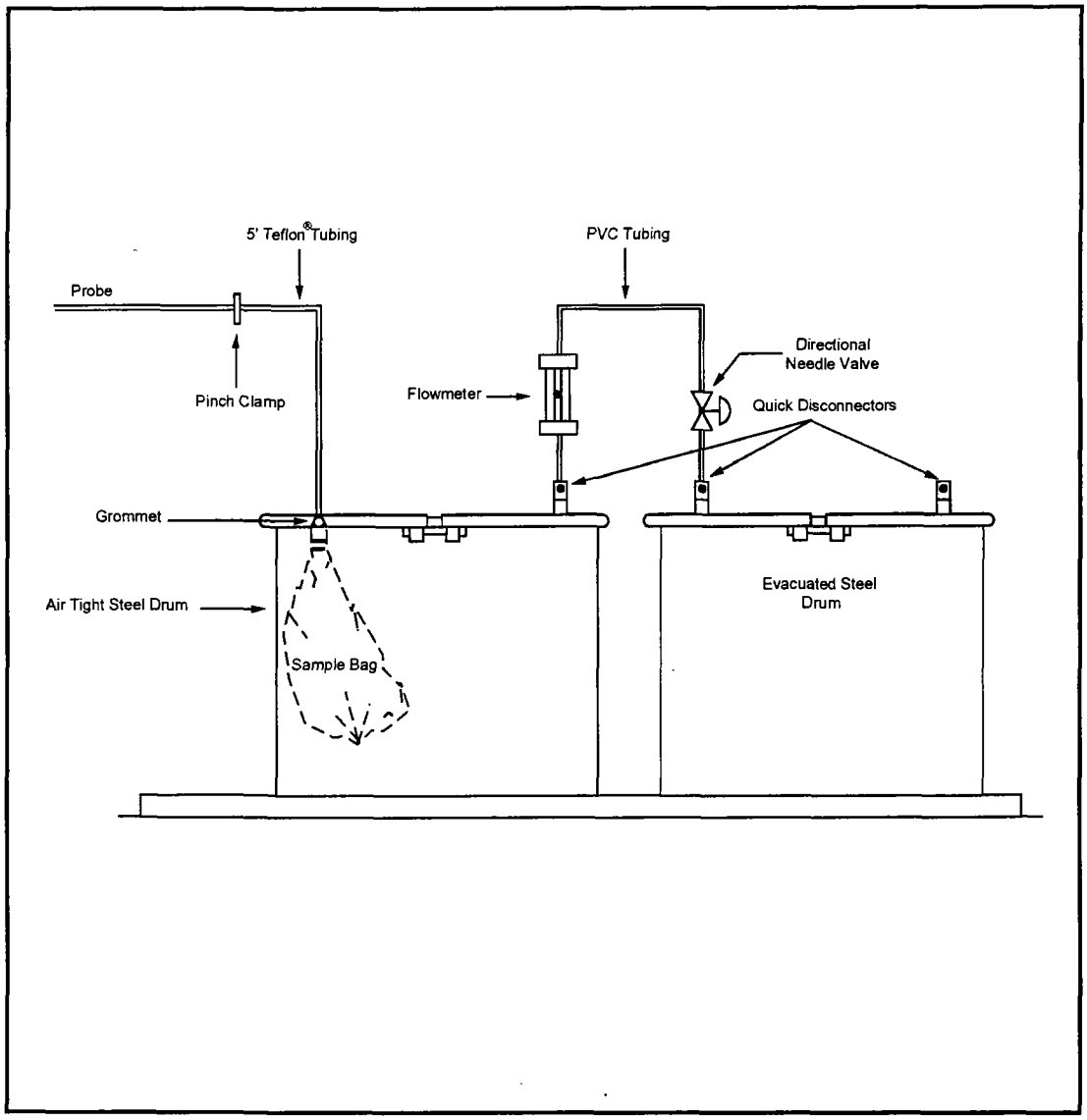

Figure 18-9a. Explosion Risk Gas Sampling Method.

Plant_____ Date_____
Site _____

	Sample_1	Sample_2	Sample_3
Source temperature (°C)			
Barometric pressure (mm Hg)			
Ambient temperature (°C)			
Sample flow rate (appr.)			
Bag number			
Start time			
Finish time			

Figure 18-10. Field sample data sheet - Tedlar bag collection method.

Plant _____ Date _____
Location _____

1. General information

Source temperature (°C)	_____
Probe temperature (°C)	_____
Ambient temperature (°C)	_____
Atmospheric pressure (mm)	_____
Source pressure ("Hg)	_____
Absolute source pressure (mm)	_____
Sampling rate (liter/min)	_____
Sample loop volume (ml)	_____
Sample loop temperature (°C)	_____
Columnar temperature:	
Initial (°C) time (min)	_____
Program rate (°C/min)	_____
Final (°C)/time (min)	_____
Carrier gas flow rate (ml/min)	_____
Detector temperature (°C)	_____
Injection time (24-hour basis)	_____
Chart speed (mm/min)	_____
Dilution gas flow rate (ml/min)	_____
Dilution gas used (symbol)	_____
Dilution ratio	_____

Figure 18-11. Field analysis data sheets.

2. Field Analysis Data - Calibration Gas

Run No. _____ Time _____

Components	Area	Attenuation	A_x_A_Factor	Conc._(ppm)

Run No. _____ Time _____

Components	Area	Attenuation	A_x_A_Factor	Conc._(ppm)

Run No. _____ Time _____

Components	Area	Attenuation	A_x_A_Factor	Conc._(ppm)

Figure 18-11 (continued). Field analysis data sheets.

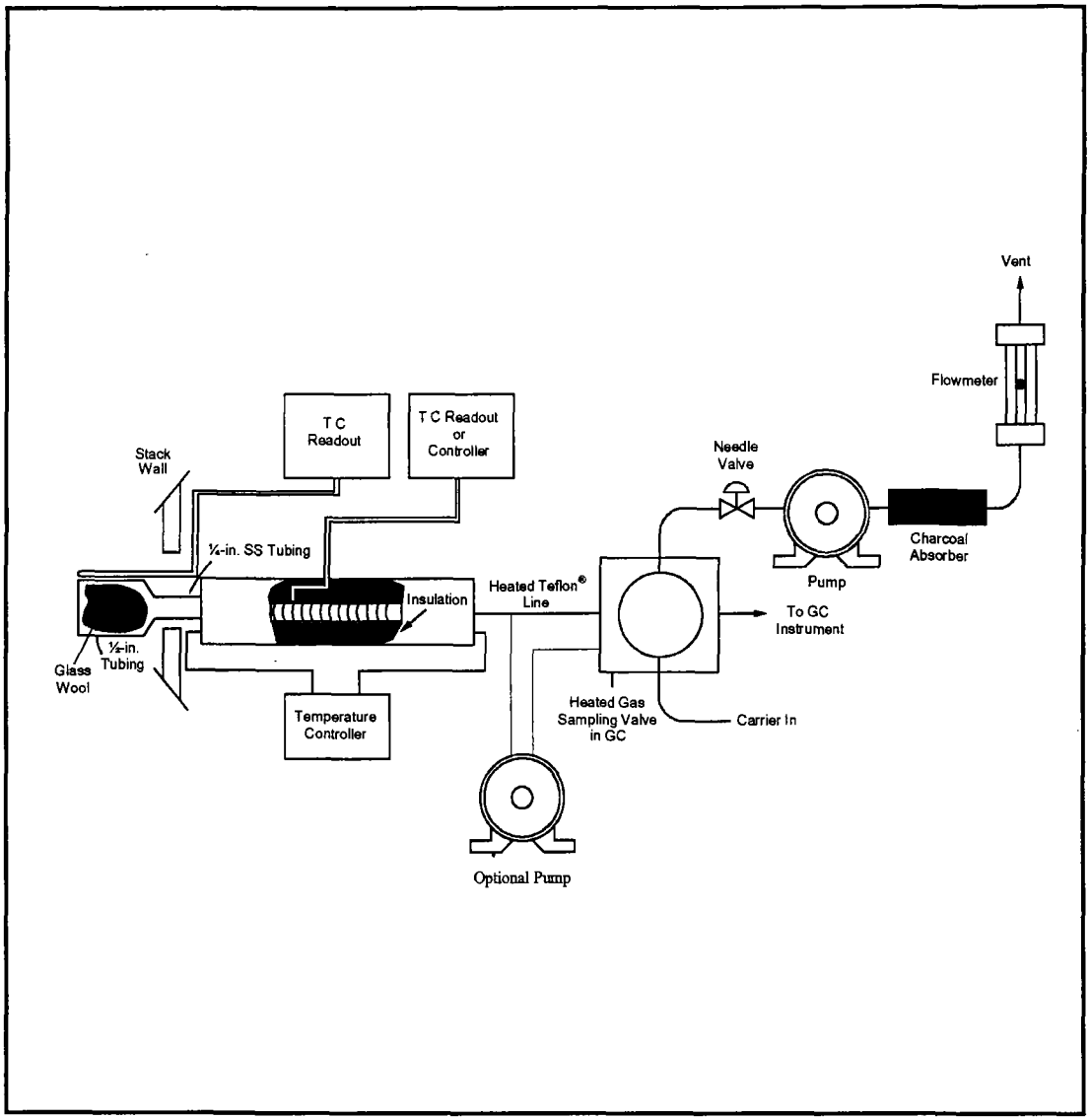

Figure 18-12. Direct Interface Sampling System.

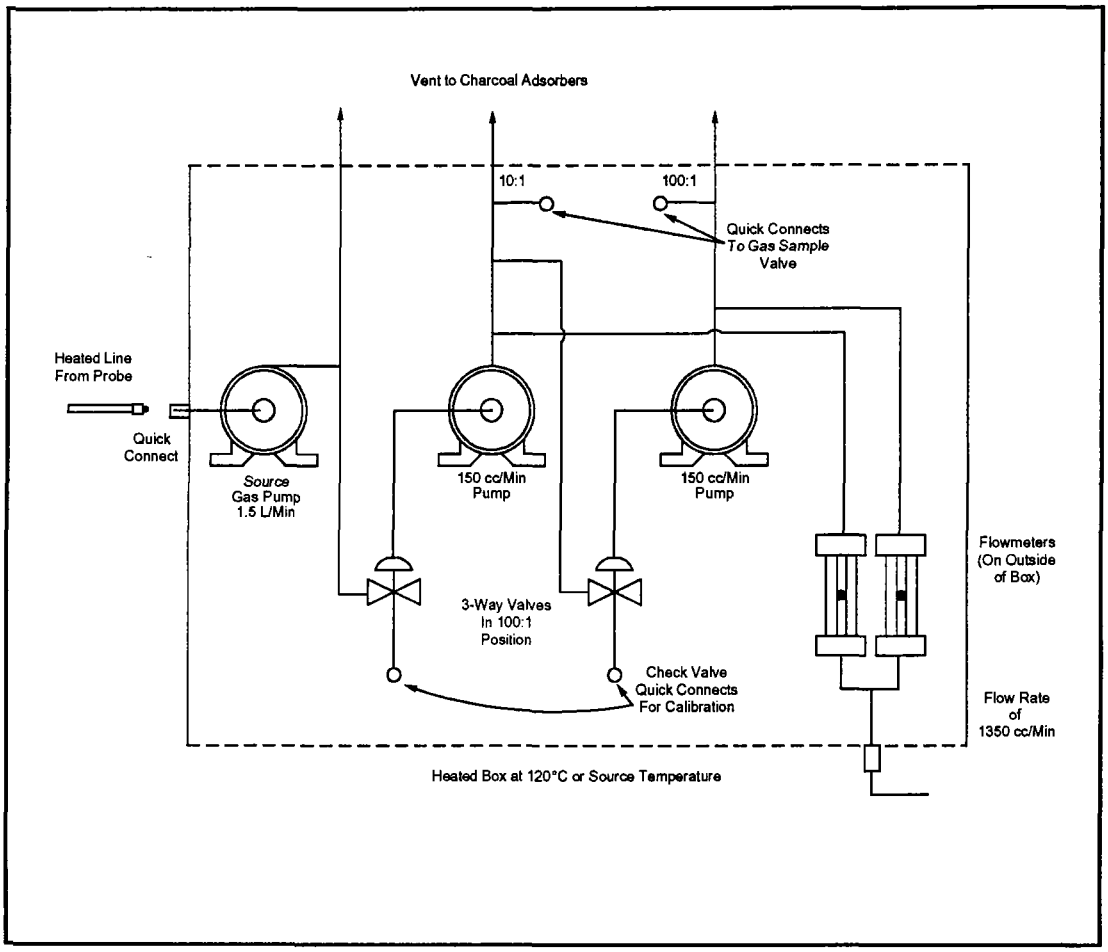

Figure 18-13. Schematic Diagram of the Heated Box Required for Dilution of Sample Gas.

Gaseous Organic Sampling and Analysis Check List
(Respond with initials or number as appropriate)

1. Presurvey data _Date_

   A. Grab sample collected |__| _____

   B. Grab sample analyzed for composition |__| _____

      Method GC |__|

      GC/MS |__|

      Other _____ |__|

   C. GC-FID analysis performed |__| _____

2. Laboratory calibration data

   A. Calibration curves prepared |__| _____

      Number of components |__|

      Number of concentrations/ component (3 required) |__|

   B. Audit samples (optional)

      Analysis completed |__| _____

      Verified for concentration |__| _____

      OK obtained for field work |__| _____

3. Sampling procedures

   A. Method

      Bag sample |__|

      Direct interface |__|

      Dilution interface |__|

   B. Number of samples collected |__| _____

4. Field Analysis

   A. Total hydrocarbon analysis performed |__| _____

   B. Calibration curve prepared |__| _____

      Number of components |__|

      Number of concentrations per |__|

component (3 required)

Gaseous Organic Sampling and Analysis Data

Plant _____

Date _____

Location _____

	Source sample_1	Source sample_2	Source sample_3
1. General information			
Source temperature (°C)	_____	_____	_____
Probe temperature (°C)	_____	_____	_____
Ambient temperature (°C)	_____	_____	_____
Atmospheric pressure (mm Hg)	_____	_____	_____
Source pressure (mm Hg)	_____	_____	_____
Sampling rate (ml/min)	_____	_____	_____
Sample loop volume (ml)	_____	_____	_____
Sample loop temperature (°C)	_____	_____	_____
Sample collection time (24-hr basis)	_____	_____	_____
Column temperature			
Initial (°C)	_____	_____	_____
Program rate (°C/min)	_____	_____	_____
Final (°C)	_____	_____	_____
Carrier gas flow rate (ml/min)	_____	_____	_____
Detector temperature (°C)	_____	_____	_____
Chart speed (cm/min)	_____	_____	_____
Dilution gas flow rate (ml/min)	_____	_____	_____
Diluent gas used (symbol)	_____	_____	_____
Dilution ratio	_____	_____	_____

Performed by:

(signature):_____ Date:_____

Figure 18-14. Sampling and analysis sheet.

METHOD 8260B
VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/
MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d_5 (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	l	nd	nd	nd	nd	pc

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	106-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d_4 (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	107-06-2	c	nd	c	c	c	c
1,2-Dichloroethane-d_4 (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	l	nd	nd	nd	nd	c
Ethanol	64-17-5	l	c	c	nd	nd	c
Ethyl acetate	141-78-6	l	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	l	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	l	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	l	nd	nd	nd	c
Methanol	67-56-1	l	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	I	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	I	nd	nd	nd	c
β-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	I	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachloroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d_8 (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
nd = Not determined
I = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene	1,3-Dichloropropane
n-Butylbenzene	2,2-Dichloropropane
sec-Butylbenzene	1,1-Dichloropropene
tert-Butylbenzene	p-Isopropyltoluene
Chloroacetonitrile	Methyl acrylate
1-Chlorobutane	Methyl-t-butyl ether
1-Chlorohexane	Pentafluorobenzene
2-Chlorotoluene	n-Propylbenzene
4-Chlorotoluene	1,2,3-Trichlorobenzene
Dibromofluoromethane	1,2,4-Trimethylbenzene
cis-1,2-Dichloroethene	1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

Injector temperature:	200 - 225°C
Transfer line temperature:	250 - 300°C

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.5 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out:	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.6 Direct split interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C 10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 260 amu
Scan time:	0.6 - 2 sec/scan
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor ($\overline{RF}$) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

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TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2'[c]	(µg/L)
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	5.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2[mc]	(µg/L)
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1 (cont.)

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2"[c]	MDL[d] (µg/L)
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06

TABLE 2 (cont.)

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

Estimated Quantitation Limits		
5-mL Ground Water Purge (µg/L)	25-mL Ground water Purge (µg/L)	Low Soil/Sediment[b] µg/kg
5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High concentration soil and sludge	125
Non-water miscible waste	500

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers" instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
β-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d_6	84	83
Bromobenzene-d_5	82	162
Bromochloromethane-d_2	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
1,1,2-Trichloroethane-d_3	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d_1	84	
Dibromofluoromethane	113	

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3

TABLE 6 (cont.)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a] Recoveries were calculated using internal standard method. The internal standard was fluorobenzene.

[b] Standard deviation was calculated by pooling data from three concentrations.

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.5	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3

TABLE 7 (cont.)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Water	Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract[a]
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Trichlorotrifluoroethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone**	105	54	2.0	5.0
Benzene	3135	44	14	0.5
Benzene-d_6	56	44	2.9	0.5
n-Butanol**	100	71	12	5.0
iso-Butanol*,**	132	27	0	5.0
Carbon tetrachloride	143	68	0	0.5
Carbon tetrachloride-^{13}C	99	44	5.1	0.5
Carbon disulfide**	95	63	0	5.0
Chlorobenzene	148	71	0	5.0
Chlorobenzene-d_5	60	44	3.6	5.0
Chloroform	149	74	0	6.0
Chloroform-d_1	51	44	2.6	6.0
1,4-Dichlorobenzene	142	72	0	7.5
1,4-Dichlorobenzene-d_4	53	44	3.4	7.5
1,2-Dichloroethane**	191	54	0	0.5
1,1-Dichloroethene*	155	51	0	0.7
1,1-Dichloroethene-d_2	68	44	3.4	0.7
Diethyl ether**	95	66	0	5.0
Ethyl acetate*,**	126	39	0	5.0
Ethylbenzene	1298	44	54	5.0
Ethylbenzene-d_{10}	63	44	3.6	5.0
Hexachloroethane	132	72	0	3.0
Hexachloroethane-^{13}C	54	45	3.5	3.0
Methylene chloride**	86	65	0.3	5.0
Methyl ethyl ketone**	107	64	0	5.0
4-Methyl-2-pentanone (MIBK)**	100	74	0.1	5.0
Nitrobenzene	111	80	0	2.0
Nitrobenzene-d_5	65	53	4.0	2.0
Pyridine**	68	85	0	5.0
Pyridine-d_5	ND	--	0	5.0
Tetrachloroethene**	101	73	0	0.7
Trichlorofluoromethane**	91	70	0	5.0
1,1,2-Cl_3F_3ethane**	81	70	0	5.0
Toluene	2881	44	128	5.0
Toluene-d_8	63	44	3.6	5.0
Trichloroethene	152	57	0	0.5
Trichloroethene-d_1	55	44	2.8	0.5

TABLE 11 (cont.)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Vinyl chloride**	100	69	0	0.2
o-Xylene	2292	44	105	5.0
o-Xylene-d_{10}	76	44	4.2	5.0
m-/p-Xylene	2583	44	253	10.0
p-Xylene-d_{10}	67	44	3.7	10.0

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

Compound	MDL (µg/L) Macro[a]	Concentration Factor Macro	Micro
Acetone	31	25-500	-
Acetonitrile	57	25-500	200
Acrolein	-	-	100
Acrylonitrile	16	25-500	100
Allyl Alcohol	7	25-500	-
1-Butanol	-	-	250
Crotonaldehyde	12	25-500	-
1,4-Dioxane	12	25-500	150
Ethyl Acetate	-	-	100
Isobutyl alcohol	7	25-500	-
Methanol	38	25-500	140
Methyl Ethyl Ketone	16	25-500	-
2-Methyl-1-propanol	-	-	250
n-Nitroso-di-n-butylamine	14	25-500	-
Paraldehyde	10	25-500	-
2-Picoline	7	25-500	-
1-Propanol	-	-	240
Propionitrile	11	25-500	200
Pyridine	4	25-500	-
o-Toluidine	13	25-500	-

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 100 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

Target Compound	Surrogate	Internal Standard
Acetone	d_6-Acetone	d_8-Isopropyl alcohol
Acetonitrile	d_3-Acetonitrile	d_8-Isopropyl alcohol
Acrylonitrile	d_8-Isopropyl alcohol	
Allyl alcohol	d_7-Dimethyl formamide	
Crotonaldehyde	d_8-Isopropyl alcohol	
1,4-Dioxane	d_8-1,4-Dioxane	d_7-Dimethyl formamide
Isobutyl alcohol	d_7-Dimethyl formamide	
Methanol	d_3-Methanol	d_8-Isopropyl alcohol
Methyl ethyl ketone	d_8-Isopropyl alcohol	
N-Nitroso-di-n-butylamine	d_7-Dimethyl formamide	
Paraldehyde	d_7-Dimethyl formamide	
2-Picoline	d_7-Dimethyl formamide	
Propionitrile	d_8-Isopropyl alcohol	
Pyridine	d_5-Pyridine	d_7-Dimethyl formamide
o-Toluidine	d_7-Dimethyl formamide	

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

Compound	Concentration(s) (ng/µL)
Internal Standards	
d_5-benzyl alcohol	10.0
d_{14}-Diglyme	10.0
d_7-Dimethyl formamide	10.0
d_8-Isopropyl alcohol	10.0
Surrogates	
d_6-Acetone	10.0
d_3-Acetonitrile	10.0
d_8-1,4-Dioxane	10.0
d_3-Methanol	10.0
d_5-Pyridine	10.0
Target Compounds	
Acetone	1.0, 5.0, 10.0, 25.0, 100.0
Acetonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Acrylonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Allyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Crotonaldehyde	1.0, 5.0, 10.0, 25.0, 100.0
1,4-Dioxane	1.0, 5.0, 10.0, 25.0, 100.0
Isobutyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Methanol	1.0, 5.0, 10.0, 25.0, 100.0
Methyl ethyl ketone	1.0, 5.0, 10.0, 25.0, 100.0
N-Nitroso-di-n-butylamine	1.0, 5.0, 10.0, 25.0, 100.0
Paraldehyde	1.0, 5.0, 10.0, 25.0, 100.0
2-Picoline	1.0, 5.0, 10.0, 25.0, 100.0
Propionitrile	1.0, 5.0, 10.0, 25.0, 100.0
Pyridine	1.0, 5.0, 10.0, 25.0, 100.0
o-Toluidine	1.0, 5.0, 10.0, 25.0, 100.0

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

Compound	Quantitation Ion[a]	Secondary Ions	Retention Time (min)[b]
Internal Standards			
d_8-Isopropyl alcohol	49		1.75
d_{14}-Diglyme	66	98,64	9.07
d_7-Dimethyl formamide	50	80	9.20
Surrogates			
d_6-Acetone	46	64,42	1.03
d_3-Methanol	33	35,30	1.75
d_3-Acetonitrile	44	42	2.63
d_8-1,4-Dioxane	96	64,34	3.97
d_5-Pyridine	84	56,79	6.73
d_5-Phenol[c]	99	71	15.43
Target Compounds			
Acetone	43	58	1.05
Methanol	31	29	1.52
Methyl ethyl ketone	43	72,57	1.53
Methacrylonitrile[c]	67	41	2.38
Acrylonitrile	53	52,51	2.53
Acetonitrile	41	40,39	2.73
Methyl isobutyl ketone[c]	85	100,58	2.78
Propionitrile	54	52,55	3.13
Crotonaldehyde	41	70	3.43
1,4-Dioxane	58	88,57	4.00
Paraldehyde	45	89	4.75
Isobutyl alcohol	43	33,42	5.05
Allyl alcohol	57	39	5.63
Pyridine	79	50,52	6.70
2-Picoline	93	66	7.27
N-Nitroso-di-n-butylamine	84	116	12.82
Aniline[c]	93	66,92	13.23
o-Toluidine	106	107	13.68
Phenol[c]	94	66,65	15.43

[a] These ions were used for quantitation in selected ion monitoring.
[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.
[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

Compound	25 ppb Spike		100 ppb Spike		500 ppb Spike	
	Mean %R	%RSD	Mean %R	%RSD	Mean %R	%RSD
d_6-Acetone	66	24	69	14	65	16
d_3-Acetonitrile	89	18	80	18	70	10
d_8-1,4-Dioxane	56	34	58	11	61	18
d_3-Methanol	43	29	48	19	56	14
d_5-Pyridine	83	6.3	84	7.8	85	9.0
Acetone	67	45	63	14	60	14
Acetonitrile	44	35	52	15	56	15
Acrylonitrile	49	42	47	27	45	27
Allyl alcohol	69	13	70	9.7	73	10
Crotonaldehyde	68	22	68	13	69	13
1,4-Dioxane	63	25	55	16	54	13
Isobutyl alcohol	66	14	66	5.7	65	7.9
Methanol	50	36	46	22	49	18
Methyl ethyl ketone	55	37	56	20	52	19
N-Nitroso-di-n-butylamine	57	21	61	15	72	18
Paraldehyde	65	20	66	11	60	8.9
Picoline	81	12	81	6.8	84	8.0
Propionitrile	67	22	69	13	68	13
Pyridine	74	7.4	72	6.7	74	7.3
o-Toluidine	52	31	54	15	58	12

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	8.0	7.5	6.7	5.4	6.6	6.8	13.0	34.2
Trichlorofluoromethane	13.3	16.5	14.9	13.0	10.3	13.6	15.2	68.0
1,1-Dichloroethene	17.1	16.7	15.1	14.8	15.6	15.9	5.7	79.2
Methylene chloride	24.5	22.7	19.7	19.4	20.6	21.4	9.1	107
trans-1,2-Dichloroethene	22.7	23.6	19.4	18.3	20.1	20.8	0.7	104
1,2-Dichloroethane	18.3	18.0	16.7	15.6	15.9	16.9	6.4	84.4
cis-1,2-Dichloroethene	26.1	23.1	22.6	20.3	20.8	22.6	9.0	113
Bromochloromethane	24.5	25.4	20.9	20.1	20.1	22.2	10.2	111
Chloroform	26.5	26.0	22.1	18.9	22.1	23.1	12.2	116
1,1,1-Trichloroethane	21.5	23.0	23.9	16.7	31.2	23.4	21.2	117
Carbon tetrachloride	23.6	24.2	22.6	18.3	23.3	22.4	9.4	112
Benzene	22.4	23.9	20.4	17.4	19.2	20.7	11.2	103
Trichloroethene	21.5	20.5	19.2	14.4	19.1	18.9	12.7	94.6
1,2-Dichloropropane	24.9	26.3	23.1	19.0	23.3	23.3	10.5	117
Dibromomethane	25.4	26.4	21.6	20.4	23.6	23.5	9.6	117
Bromodichloromethane	25.7	26.7	24.1	17.9	23.0	23.5	13.1	117
Toluene	28.3	25.0	24.8	16.3	23.6	23.6	16.9	118
1,1,2-Trichloroethane	25.4	24.5	21.6	17.7	22.1	22.2	12.1	111
1,3-Dichloropropane	25.4	24.2	22.7	17.0	22.2	22.3	12.8	112
Dibromochloromethane	26.3	26.2	23.7	18.2	23.2	23.5	12.5	118
Chlorobenzene	22.9	22.5	19.8	14.6	19.4	19.9	15.0	99.3
1,1,1,2-Tetrachloroethane	22.4	27.7	25.1	19.4	22.6	23.4	12.0	117
Ethylbenzene	25.6	25.0	22.1	14.9	24.0	22.3	17.5	112
p-Xylene	22.5	22.0	19.8	13.9	20.3	19.7	15.7	98.5
o-Xylene	24.2	23.1	21.6	14.0	20.4	20.7	17.3	103
Styrene	23.9	21.5	20.9	14.3	20.5	20.2	15.7	101
Bromoform	26.8	25.6	26.0	20.1	23.5	24.4	9.9	122
iso-Propylbenzene	25.3	25.1	24.2	15.4	24.6	22.9	16.6	114
Bromobenzene	19.9	21.8	20.0	15.5	19.1	19.3	10.7	96.3
1,2,3-Trichloropropane	25.9	23.0	25.6	15.9	21.4	22.2	15.8	111
n-Propylbenzene	26.0	23.8	22.6	13.9	21.9	21.6	19.0	106
2-Chlorotoluene	23.6	23.8	21.3	13.0	21.5	20.6	19.2	103
4-Chlorotoluene	21.0	19.7	18.4	12.1	18.3	17.9	17.1	89.5
1,3,5-Trimethylbenzene	24.0	22.1	22.5	13.8	22.9	21.1	17.6	105
sec-Butylbenzene	25.9	25.3	27.8	16.1	28.6	24.7	18.1	124
1,2,4-Trimethylbenzene	30.6	39.2	22.4	18.0	22.7	26.6	28.2	133
1,3-Dichlorobenzene	20.3	20.6	18.2	13.0	17.6	17.9	15.2	89.7
p-iso-Propyltoluene	21.6	22.1	21.6	16.0	22.8	20.8	11.8	104
1,4-Dichlorobenzene	18.1	21.2	20.0	13.2	17.4	18.0	15.3	90.0
1,2-Dichlorobenzene	18.4	22.5	22.5	15.2	19.9	19.7	13.9	96.6
n-Butylbenzene	13.1	20.3	19.5	10.8	18.7	16.5	23.1	82.4
1,2,4-Trichlorobenzene	14.5	14.9	15.7	8.8	12.3	13.3	18.8	66.2
Hexachlorobutadiene	17.6	22.5	21.6	13.2	21.6	19.3	18.2	96.3
1,2,3-Trichlorobenzene	14.9	15.9	16.5	11.9	13.9	14.6	11.3	73.1

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	33.4	31.0	30.9	29.7	28.6	30.8	5.2	154
Trichlorofluoromethane	37.7	20.8	20.0	21.8	20.5	24.1	28.2	121
1,1-Dichloroethene	21.7	33.5	39.8	30.2	32.5	31.6	18.5	158
Methylene chloride	20.9	19.4	18.7	18.3	18.4	19.1	5.1	95.7
trans-1,2-Dichloroethene	21.8	18.9	20.4	17.9	17.8	19.4	7.9	96.8
1,1-Dichloroethane	23.8	21.9	21.3	21.3	20.5	21.8	5.2	109
cis-1,2-Dichloroethene	21.6	18.8	18.5	18.2	18.2	19.0	6.7	95.2
Bromochloromethane	22.3	19.5	19.3	19.0	19.2	20.0	6.0	100
Chloroform	20.5	17.1	17.3	16.5	15.9	17.5	9.2	87.3
1,1,1-Trichloroethane	16.4	11.9	10.7	9.5	9.4	11.6	22.4	57.8
Carbon tetrachloride	13.1	11.3	13.0	11.8	11.2	12.1	6.7	60.5
Benzene	21.1	19.3	18.7	18.2	16.9	18.8	7.4	94.1
Trichloroethene	19.6	16.4	16.5	16.5	15.5	16.9	8.3	84.5
1,2-Dichloropropane	21.8	19.0	18.3	18.8	16.5	18.9	9.0	94.4
Dibromomethane	20.9	17.9	17.9	17.2	18.3	18.4	6.9	92.1
Bromodichloromethane	20.9	18.0	18.9	18.2	17.3	18.6	6.6	93.2
Toluene	22.2	17.3	18.8	17.0	15.9	18.2	12.0	91.2
1,1,2-Trichloroethane	21.0	16.5	17.2	17.2	16.5	17.7	9.6	88.4
1,3-Dichloropropane	21.4	17.3	18.7	18.6	16.7	18.5	8.8	92.6
Dibromochloromethane	20.9	18.1	19.0	18.8	16.6	18.7	7.5	93.3
Chlorobenzene	20.8	18.4	17.6	16.8	14.8	17.7	11.2	88.4
1,1,1,2-Tetrachloroethane	19.5	19.0	17.8	17.2	16.5	18.0	6.2	90.0
Ethylbenzene	21.1	18.3	18.5	16.9	15.3	18.0	10.6	90.0
p-Xylene	20.0	17.4	18.2	16.3	14.4	17.3	10.9	86.3
o-Xylene	20.7	17.2	16.8	16.2	14.8	17.1	11.4	85.7
Styrene	18.3	15.9	16.2	15.3	13.7	15.9	9.3	79.3
Bromoform	20.1	15.9	17.1	17.5	16.1	17.3	8.6	86.7
iso-Propylbenzene	21.0	18.1	19.2	18.4	15.6	18.4	9.6	92.2
Bromobenzene	20.4	16.2	17.2	16.7	15.4	17.2	10.1	85.9
1,1,2,2-Tetrachloroethane	23.3	17.9	21.2	18.8	16.8	19.6	12.1	96.0
1,2,3-Trichloropropane	18.4	14.6	15.6	16.1	15.6	16.1	8.0	80.3
n-Propylbenzene	20.4	18.9	17.9	17.0	14.3	17.7	11.6	88.4
2-Chlorotoluene	19.1	17.3	16.1	16.0	14.4	16.7	9.2	83.6
4-Chlorotoluene	19.0	15.5	16.8	15.9	13.6	16.4	10.6	81.8
1,3,5-Trimethylbenzene	20.8	18.0	17.4	16.1	14.7	17.4	11.7	86.9
sec-Butylbenzene	21.4	18.3	18.9	17.0	14.9	18.1	11.8	90.5
1,2,4-Trimethylbenzene	20.5	18.6	16.8	15.3	13.7	17.0	14.1	85.0
1,3-Dichlorobenzene	17.6	15.9	15.6	14.2	14.4	15.6	7.9	77.8
p-iso-Propyltoluene	20.5	17.0	17.1	15.6	13.4	16.7	13.9	83.6
1,4-Dichlorobenzene	18.5	13.8	14.8	16.7	14.9	15.7	10.5	78.7
1,2-Dichlorobenzene	18.4	15.0	15.4	15.3	13.5	15.5	10.5	77.6
n-Butylbenzene	19.6	15.9	15.9	14.4	18.9	16.9	11.7	84.6
1,2,4-Trichlorobenzene	15.2	17.2	17.4	13.6	12.1	15.1	13.5	75.4
Hexachlorobutadiene	18.7	16.2	15.5	13.8	16.6	16.1	10.0	80.7
Naphthalene	13.9	11.1	10.2	10.8	11.4	11.5	11.0	57.4
1,2,3-Trichlorobenzene	14.9	15.2	16.8	13.7	12.7	14.7	9.5	73.2

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	12.7	10.9	9.8	8.1	7.2	9.7	20.2	48.7
Trichlorofluoromethane	33.7	6.4	30.3	27.8	22.9	24.2	39.6	121
1,1-Dichloroethene	27.7	20.5	24.1	15.1	13.2	20.1	26.9	101
Methylene chloride	25.4	23.9	24.7	22.2	24.2	24.1	4.4	120
trans-1,2-Dichloroethene	2.8	3.0	3.3	2.2	2.4	2.7	15.0	13.6
1,1-Dichloroethane	24.1	26.3	27.0	20.5	21.2	23.8	11.0	119
cis-1,2-Dichloroethene	8.3	10.2	8.7	5.8	6.4	7.9	20.1	39.4
Bromochloromethane	11.1	11.8	10.2	8.8	9.0	10.2	11.2	50.9
Chloroform	16.7	16.9	17.0	13.8	15.0	15.9	7.9	79.3
1,1,1-Trichloroethane	24.6	22.8	22.1	16.2	20.9	21.3	13.4	107
Carbon tetrachloride	19.4	20.3	22.2	20.0	20.2	20.4	4.6	102
Benzene	21.4	22.0	22.4	19.6	20.4	21.2	4.9	106
Trichloroethene	12.4	16.5	14.9	9.0	9.9	12.5	22.9	62.7
1,2-Dichloropropane	19.0	18.8	19.7	16.0	17.6	18.2	7.1	91.0
Dibromomethane	7.3	8.0	6.9	5.6	6.8	6.9	11.3	34.6
Bromodichloromethane	14.9	15.9	15.9	12.8	13.9	14.7	8.3	73.3
Toluene	42.6	39.3	45.1	39.9	45.3	42.4	5.9	212
1,1,2-Trichloroethane	13.9	15.2	1.4	21.3	14.9	15.9	17.0	79.6
1,3-Dichloropropane	13.3	16.7	11.3	10.9	9.5	12.3	20.3	61.7
Dibromochloromethane	14.5	13.1	14.5	11.9	14.4	13.7	7.6	68.3
Chlorobenzene	8.4	10.0	8.3	6.9	7.8	8.3	12.1	41.3
1,1,1,2-Tetrachloroethane	16.7	16.7	15.6	15.8	15.7	16.1	3.2	80.4
Ethylbenzene	22.1	21.4	23.1	20.1	22.6	21.9	4.8	109
p-Xylene	41.4	38.4	43.8	38.3	44.0	41.2	6.1	206
o-Xylene	31.7	30.8	34.3	30.4	33.2	32.1	4.6	160
Styrene	0	0	0	0	0	0	0	0
Bromoform	8.6	8.9	9.1	7.0	7.7	8.3	9.4	41.4
iso-Propylbenzene	18.1	18.8	9.7	18.3	19.6	18.9	3.5	94.4
Bromobenzene	5.1	5.4	5.3	4.4	4.0	4.8	11.6	24.1
1,1,2,2-Tetrachloroethane	14.0	13.5	14.7	15.3	17.1	14.9	8.5	74.5
1,2,3-Trichloropropane	11.0	12.7	11.7	11.7	11.9	11.8	4.5	59.0
n-Propylbenzene	13.4	13.3	14.7	12.8	13.9	13.6	4.7	68.1
2-Chlorotoluene	8.3	9.0	11.7	8.7	7.9	9.1	14.8	45.6
4-Chlorotoluene	5.1	5.4	5.5	4.8	4.5	5.0	7.9	25.2
1,3,5-Trimethylbenzene	31.3	27.5	33.0	31.1	33.6	31.3	6.8	157
sec-Butylbenzene	13.5	13.4	16.4	13.8	15.4	14.5	8.3	72.5
1,2,4-Trimethylbenzene	38.7	32.4	40.8	34.1	40.3	37.3	9.1	186
1,3-Dichlorobenzene	3.6	3.6	3.7	3.0	3.2	3.4	8.0	17.2
p-iso-Propyltoluene	14.7	14.1	16.1	13.9	15.1	14.8	5.2	73.8
1,4-Dichlorobenzene	3.0	3.5	3.3	2.6	2.8	3.0	10.2	15.0
1,2-Dichlorobenzene	3.6	4.3	4.0	3.5	3.6	3.8	8.3	19.0
n-Butylbenzene	17.4	13.8	14.0	18.9	24.0	17.6	21.2	88.0
1,2,4-Trichlorobenzene	2.8	2.9	3.3	2.6	3.2	3.0	8.5	15.0
Hexachlorobutadiene	4.8	4.0	6.1	5.6	6.0	5.3	15.1	26.4
Naphthalene	5.5	5.1	5.5	4.7	5.6	5.3	6.2	26.5
1,2,3-Trichlorobenzene	2.2	2.3	2.4	2.2	2.3	2.3	3.5	11.4

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Soil/H_2O[b] Recovery Mean	RSD	Soil/Oil[c] Recovery Mean	RSD	Soil/Oil/H_2O Recovery Mean	RSD
Chloromethane	61	20	40	18	108	68
Bromomethane	58	20	47	13	74	13
Vinyl chloride	54	12	46	11	72	20
Chloroethane	46	10	41	8	52	14
Methylene chloride	60	2	65	8	76	11
Acetone	INT[e]	INT	44	8		
Carbon disulfide	47	13	53	10	47	4
1,1-Dichloroethene	48	9	47	5	58	3
1,1-Dichloroethane	61	6	58	9	61	6
trans-1,2-Trichloroethane	54	7	60	7	56	5
cis-1,2-Dichloroethene	60	4	72	6	63	8
Chloroform	104	11	93	6	114	15
1,2-Dichloroethane	177	50	117	8	151	22
2-Butanone	INT	36	38	INT		
1,1,1-Trichloroethane	124	13	72	16	134	26
Carbon tetrachloride	172	122	INT	INT		
Vinyl acetate	88	11	INT			
Bromodichloromethane	93	4	91	23	104	23
1,1,2,2-Tetrachloroethane	96	13	50	12	104	7
1,2-Dichloropropane	105	8	102	6	111	6
trans-1,3-Dichloropropene	134	10	84	16	107	8
Trichloroethene	98	9	99	10	100	5
Dibromochloromethane	119	8	125	31	142	16
1,1,2-Trichloroethane	126	10	72	16	97	4
Benzene	99	7	CONT[f]	CONT		
cis-1,3-Dichloropropene	123	12	94	13	112	9
Bromoform	131	13	58	18	102	9
2-Hexanone	155	18	164	19	173	29
4-Methyl-2-pentanone	152	20	185	20	169	18
Tetrachloroethene	90	9	123	14	128	7
Toluene	94	3	CONT	CONT		
Chlorobenzene	98	7	93	18	112	5
Ethylbenzene	114	13	CONT	CONT		
Styrene	106	8	93	18	112	5
p-Xylene	97	9	CONT	CONT		
o-Xylene	105	8	112	12	144	13

TABLE 20 (cont.)

Compound	Soil/H_2O[b] Recovery Mean	RSD	Soil/Oil[c] Recovery Mean	RSD	Soil/Oil/H_2O Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	177	50	117	8	151	22
Toluene-d_8	96	6	79	12	82	6
Bromofluorobenzene	139	13	37	13	62	5

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Efficiency Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	CONT[c]	
Acetone	CONT[c]	
Carbon disulfide	79	36
1,1-Dichloroethene	122	39
1,1-Dichloroethane	126	35
trans-1,2-Trichloroethene	109	46
cis-1,2-Dichloroethene	106	22
Chloroform	111	32
1,2-Dichloroethane	117	27
2-Butanone	INT[d]	
1,1,1-Trichloroethane	106	30
Carbon tetrachloride	83	34
Vinyl acetate	INT[d]	
Bromodichloromethane	97	22
1,1,2,2-Tetrachloroethane	67	20
1,2-Dichloropropane	117	23
trans-1,3-Dichloropropene	92	22
Trichloroethene	98	31
Dibromochloromethane	71	19
1,1,2-Trichloroethane	92	20
Benzene	129	35
cis-1,3-Dichloropropene	102	24
Bromoform	58	19
2-Hexanone	INT[d]	
4-Methyl-2-pentanone	113	37
Tetrachloroethene	66	20
Toluene	CONT[c]	
Chlorobenzene	65	19
Ethylbenzene	74	19
Styrene	57	14
p-Xylene	46	13
o-Xylene	83	20

TABLE 21 (cont.)

Compound	Efficiency Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	115	27
Toluene-d_8	88	24
Bromofluorobenzene	52	15

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	7.8	7.3
Bromomethane	9.7	9.8
Vinyl chloride	*9.5*	*9.4*
Chloroethane	9.2	10.0
Methylene chloride	CONT[b]	CONT[b]
Acetone	CONT[b]	CONT[b]
Carbon disulfide	5.4	4.9
1,1-Dichloroethene	4.0	5.7
1,1-Dichloroethane	4.0	3.5
trans-1,2-Dichloroethene	4.4	4.0
cis-1,2-Dichloroethene	4.7	4.1
Chloroform	5.6	5.0
1,2-Dichloroethane	3.3	3.2
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	1.1	4.2
Carbon tetrachloride	3.2	3.5
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	3.2	2.8
1,1,2,2-Tetrachloroethane	4.4	3.8
1,2-Dichloropropane	3.8	3.7
trans-1,3-Dichloropropene	3.4	3.0
Trichloroethene	3.1	4.0
Dibromochloromethane	3.5	3.2
1,1,2-Trichloroethane	4.4	3.3
Benzene	3.6	3.2
cis-1,3-Dichloropropene	3.5	3.0
Bromoform	4.9	4.0
2-Hexanone	7.7	8.0
4-Methyl-2-pentanone	7.5	8.0
Tetrachloroethene	4.3	4.0
Toluene	3.0	2.5
Chlorobenzene	3.3	2.8
Ethylbenzene	3.6	3.5
Styrene	3.5	3.3
p-Xylene	3.7	3.5
o-Xylene	3.3	4.7

Footnotes are on the following page.

TABLE 22 (cont.)

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Chloromethane	114	27	116	29	176	67
Bromomethane	131	14	121	14	113	21
Vinyl chloride	131	13	120	16	116	23
Chloroethane	110	15	99	8	96	16
Methylene chloride	87	16	105	15	77	6
Acetone	83	22	65	34	119	68
Carbon disulfide	138	17	133	23	99	47
1,1-Dichloroethene	105	11	89	4	96	18
1,1-Dichloroethane	118	10	119	11	103	25
trans-1,2-Dichloroethene	105	11	107	14	96	18
cis-1,2-Dichloroethene	106	7	99	5	104	23
Chloroform	114	6	104	8	107	21
1,2-Dichloroethane	104	6	109	8	144	19
2-Butanone	83	50	106	31	INT[c]	
1,1,1-Trichloroethane	118	9	109	9	113	23
Carbon tetrachloride	102	6	108	12	109	27
Vinyl acetate	90	16	99	7	72	36
Bromodichloromethane	104	3	110	5	99	5
1,1,2,2-Tetrachloroethane	85	17	81	7	111	43
1,2-Dichloropropane	100	6	103	2	104	7
trans-1,3-Dichloropropene	105	8	105	4	92	4
Trichloroethene	98	4	99	2	95	5
Dibromochloroethane	99	8	99	6	90	25
1,1,2-Trichloroethane	98	7	100	4	76	12
Benzene	97	4	100	5	112	10
cis-1,3-Dichloropropene	106	5	105	4	98	3
Bromoform	93	16	94	8	57	21
2-Hexanone	60	17	63	16	78	23
4-Methyl-2-pentanone	79	24	63	14	68	15
Tetrachloroethene	101	3	97	7	77	14
Toluene	100	6	97	8	85	5
Chlorobenzene	98	6	98	4	88	16
Ethylbenzene	100	3	92	8	73	13
Styrene	98	4	97	9	88	16
p-Xylene	96	4	94	8	60	12
o-Xylene	96	7	95	6	72	14

TABLE 23 (*cont.*)

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	104	6	109	6	144	19
Toluene-d_8	104	5	102	2	76	7
Bromofluorobenzene	106	6	106	9	40	8

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.2	8.0	7.3	N/A[f]
Bromomethane	2.8	4.9	9.8	N/A[f]
Vinyl chloride	3.5	6.0	9.4	N/A[f]
Chloroethane	5.9	6.0	10.0	N/A[f]
Methylene chloride	3.1	4.0	CONT[g]	0.05
Acetone	5.6	CONT[g]	CONT[g]	0.06
Carbon disulfide	2.5	2.0	4.9	0.18
1,1-Dichloroethene	2.9	3.2	5.7	0.18
1,1-Dichloroethane	2.2	2.0	3.5	0.14
trans-1,2-Dichloroethene	2.2	1.4	4.0	0.10
cis-1,2-Dichloroethene	2.0	2.3	4.1	0.07
Chloroform	2.4	1.8	5.0	0.07
1,2-Dichloroethane	1.7	1.5	3.2	0.06
2-Butanone	7.4	INT[h]	INT[h]	INT[h]
1,1,1-Trichloroethane	1.8	1.7	4.2	0.10
Carbon tetrachloride	1.4	1.5	3.5	0.13
Vinyl acetate	11.8	INT[h]	INT[h]	INT[h]
Bromodichloromethane	1.6	1.4	2.8	0.06
1,1,2,2-Tetrachloroethane	2.5	2.1	3.8	0.02
1,2-Dichloropropane	2.2	2.1	3.7	0.15
trans-1,3-Dichloropropene	1.5	1.7	3.0	0.05
Trichloroethene	1.6	1.7	4.0	0.04
Dibromochloromethane	1.7	1.5	3.2	0.07
1,1,2-Trichloroethane	2.1	1.7	3.3	0.05
Benzene	0.5	1.5	3.2	0.05
cis-1,3-Dichloropropene	1.4	1.7	3.0	0.04
Bromoform	1.8	1.5	4.0	0.05
2-Hexanone	4.6	3.6	8.0	INT[h]
4-Methyl-2-pentanone	3.5	4.6	8.0	INT[h]
Tetrachloroethene	1.4	1.6	4.0	0.10
Toluene	1.0	3.3	2.5	0.05
Chlorobenzene	1.4	1.4	2.8	0.06
Ethylbenzene	1.5	2.8	3.5	0.04
Styrene	1.4	1.4	3.3	0.18
p-Xylene	1.5	2.9	3.5	0.20
o-Xylene	1.7	3.4	4.7	0.07

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES
(METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.1	8.6[f]	7.8	N/A[g]
Bromomethane	2.5	4.9[f]	9.7	N/A[g]
Vinyl chloride	4.0	7.1[f]	9.5	N/A[g]
Chloroethane	6.1	7.5[f]	9.2	N/A[g]
Methylene chloride	3.1	3.3	CONT[h]	0.08
Acetone	33.0[f]	CONT[h]	CONT[h]	0.12
Carbon disulfide	2.5	3.2	5.4	0.19
1,1-Dichloroethene	3.4	3.8	4.0	0.19
1,1-Dichloroethane	2.3	1.7	4.0	0.13
trans-1,2-Dichloroethene	3.0	3.2	4.4	0.09
cis-1,2-Dichloroethene	2.4	2.7	4.7	0.08
Chloroform	2.7	2.6	5.6	0.06
1,2-Dichloroethane	1.6	1.7	3.3	0.06
2-Butanone	57.0[f]	INT[i]	INT[i]	INT[i]
1,1,1-Trichloroethane	1.6	2.4	1.1	0.08
Carbon tetrachloride	1.5	1.7	3.2	0.15
Vinyl acetate	23.0[f]	INT[i]	INT[i]	INT[i]
Bromodichloromethane	2.0	2.3	3.2	0.05
1,1,2,2-Tetrachloroethane	3.6	3.2	4.4	0.09
1,2-Dichloropropane	2.9	3.7	3.8	0.12
trans-1,3-Dichloropropene	2.3	2.4	3.8	0.08
Trichloroethene	2.5	3.0	3.1	0.06
Dibromochloromethane	2.1	2.9	3.5	0.04
1,1,2-Trichloroethane	2.7	2.8	4.4	0.07
Benzene	1.7	2.9	3.6	0.03
cis-1,3-Dichloropropene	2.1	2.5	3.5	0.06
Bromoform	2.3	2.5	4.9	0.10
2-Hexanone	4.6	4.6	7.7	INT[i]
4-Methyl-2-pentanone	3.8	3.9	7.5	INT[i]
Tetrachloroethene	1.8	2.6	4.3	0.12
Toluene	1.8	4.4	3.0	0.09
Chlorobenzene	2.4	2.6	3.3	0.07
Ethylbenzene	2.4	4.1	3.6	0.09
Styrene	2.0	2.5	3.5	0.16
p-Xylene	2.3	3.9	3.7	0.18
o-Xylene	2.4	4.1	3.3	0.08

TABLE 25 (cont.)

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

[h] Contamination of sample by analyte prevented determination.

[i] Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL
USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Recovery Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	62	32
Acetone	108	55
Carbon disulfide	98	46
1,1-Dichloroethene	97	24
1,1-Dichloroethane	96	22
trans-1,2-Trichloroethene	86	23
cis-1,2-Dichloroethene	99	11
Chloroform	93	14
1,2-Dichloroethane	138	31
2-Butanone	INT[c]	
1,1,1-Trichloroethane	89	14
Carbon tetrachloride	129	23
Vinyl acetate	INT[c]	
Bromodichloromethane	106	14
1,1,2,2-Tetrachloroethane	205	46
1,2-Dichloropropane	107	24
trans-1,3-Dichloropropene	98	13
Trichloroethene	102	8
Dibromochloromethane	168	21
1,1,2-Trichloroethane	95	7
Benzene	146	10
cis-1,3-Dichloropropene	98	11
Bromoform	94	18
2-Hexanone	INT[c]	
4-Methyl-2-pentanone	INT[c]	
Tetrachloroethene	117	22
Toluene	108	8
Chlorobenzene	101	12
Ethylbenzene	96	10
Styrene	120	46
p-Xylene	87	23
o-Xylene	90	10

TABLE 26 (cont.)

Compound	Recovery Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	137	30
Toluene-d_8	84	6
Bromofluorobenzene	48	2

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	N/A[b]	N/A[b]
Bromomethane	N/A[b]	N/A[b]
Vinyl chloride	N/A[b]	N/A[b]
Chloroethane	N/A[b]	N/A[b]
Methylene chloride	80	50
Acetone	120	60
Carbon disulfide	190	180
1,1-Dichloroethene	190	180
1,1-Dichloroethane	130	140
trans-1,2-Dichloroethene	90	100
cis-1,2-Dichloroethene	80	70
Chloroform	60	70
1,2-Dichloroethane	60	60
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	80	100
Carbon tetrachloride	150	130
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	50	60
1,1,2,2-Tetrachloroethane	90	20
1,2-Dichloropropane	120	150
trans-1,3-Dichloropropene	80	50
Trichloroethene	60	40
Dibromochloromethane	40	70
1,1,2-Trichloroethane	70	50
Benzene	30	50
cis-1,3-Dichloropropene	60	40
Bromoform	100	50
2-Hexanone	INT[c]	INT[c]
4-Methyl-2-pentanone	INT[c]	INT[c]
Tetrachloroethene	120	100
Toluene	90	50
Chlorobenzene	70	60
Ethylbenzene	90	40
Styrene	160	180
p-Xylene	180	200
o-Xylene	80	70

TABLE 27 (cont.)

[a] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] No analyses.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

Chloroform-d_1	1,1,2-TCA-d_3	Bromobenzene-d_5
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Chloromethane	1,1-Dichloropropene	Bromoform
Vinyl chloride	Carbon tetrachloride	Styrene
Bromomethane	Benzene	iso-Propylbenzene
Chloroethane	Dibromomethane	Bromobenzene
Trichlorofluoromethane	1,2-Dichloropropane	n-Propylbenzene
1,1-Dichloroethene	Trichloroethene	2-Chlorotoluene
Methylene chloride	Bromodichloromethane	4-Chlorotoluene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	tert-Butylbenzene
cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,4-Trimethylbenzene
Bromochloromethane	Toluene	sec-Butylbenzene
Chloroform	1,3-Dichloropropane	1,3-Dichlorobenzene
2,2-Dichloropropane	Dibromochloromethane	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dibromoethane	p-iso-Propyltoluene
	Tetrachloroethene	1,2-Dichlorobenzene
	1,1,2-Trichloroethane	n-Butylbenzene
	Ethylbenzene	1,2-Dibromo-3-chloropropane
	m-Xylene	1,2,4-Trichlorobenzene
	p-Xylene	Naphthalene
	o-Xylene	Hexachlorobutadiene
	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
	1,2,3-Trichloropropane	

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

Compound	% RSD	MDL (µg/kg)
Benzene	3.0	0.34
Bromochloromethane	3.4	0.27
Bromodichloromethane	2.4	0.21
Bromoform	3.9	0.30
Bromomethane	11.6	1.3
Carbon tetrachloride	3.6	0.32
Chlorobenzene	3.2	0.24
Chloroethane	5.6	0.51
Chloroform	3.1	0.30
Chloromethane	4.1	3.5[b]
1,2-Dibromo-3-chloropropane	5.7	0.40
1,2-Dibromoethane	3.2	0.29
Dibromomethane	2.8	0.20
1,2-Dichlorobenzene	3.3	0.27
1,3-Dichlorobenzene	3.4	0.24
1,4-Dichlorobenzene	3.7	0.30
Dichlorodifluoromethane	3.0	0.28
1,1-Dichloroethane	4.5	0.41
1,2-Dichloroethane	3.0	0.24
1,1-Dichloroethene	3.3	0.28
cis-1,2-Dichloroethene	3.2	0.27
trans-1,2-Dichloroethene	2.6	0.22
1,2-Dichloropropane	2.6	0.21
1,1-Dichloropropene	3.2	0.30
cis-1,3-Dichloropropene	3.4	0.27
Ethylbenzene	4.8	0.47
Hexachlorobutadiene	4.1	0.38
Methylene chloride	8.2	0.62[c]
Naphthalene	16.8	3.4[c]
Styrene	7.9	0.62
1,1,1,2-Tetrachloroethane	3.6	0.27
1,1,2,2-Tetrachloroethane	2.6	0.20
Tetrachloroethene	9.8	1.2[c]
Toluene	3.5	0.38
1,2,4-Trichlorobenzene	4.2	0.44
1,1,1-Trichloroethane	2.7	0.27
1,1,2-Trichloroethane	2.6	0.20
Trichloroethene	2.3	0.19

TABLE 29 (cont.)

Compound	% RSD	MDL (µg/kg)
Trichlorofluoromethane	2.7	0.31
1,2,3-Trichloropropane	1.5	0.11
Vinyl chloride	4.8	0.45
m-Xylene/p-Xylene	3.6	0.37
o-Xylene	3.6	0.33

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Benzene	37.6	35.2	38.4	37.1	3.7	185[a]
Bromochloromethane	20.5	19.4	20.0	20.0	2.3	100
Bromodichloromethane	21.1	20.3	22.8	21.4	4.9	107
Bromoform	23.8	23.9	25.1	24.3	2.4	121
Bromomethane	21.4	19.5	19.7	20.2	4.2	101
Carbon tetrachloride	27.5	26.6	28.6	27.6	3.0	138
Chlorobenzene	25.6	25.4	26.4	25.8	1.7	129
Chloroethane	25.0	24.4	25.3	24.9	1.5	125
Chloroform	21.9	20.9	21.7	21.5	2.0	108
Chloromethane	21.0	19.9	21.3	20.7	2.9	104[a]
1,2-Dibromo-3-chloro-propane	20.8	20.8	21.0	20.9	0.5	104
1,2-Dibromoethane	20.1	19.5	20.6	20.1	2.2	100
Dibromomethane	22.2	21.0	22.8	22.0	3.4	110
1,2-Dichlorobenzene	18.0	17.7	17.1	17.6	2.1	88.0
1,3-Dichlorobenzene	21.2	21.0	20.1	20.8	2.3	104
1,4-Dichlorobenzene	20.1	20.9	19.9	20.3	2.1	102
Dichlorodifluoromethane	25.3	24.1	25.4	24.9	2.4	125
1,1-Dichloroethane	23.0	22.0	22.7	22.6	1.9	113
1,2-Dichloroethane	20.6	19.5	19.8	20.0	2.3	100
1,1-Dichloroethene	24.8	23.8	24.4	24.3	1.7	122
cis-1,2-Dichloroethene	21.6	20.0	21.6	21.1	3.6	105
trans-1,2-Dichloroethene	22.4	21.4	22.2	22.0	2.0	110
1,2-Dichloropropane	22.8	22.2	23.4	22.8	2.1	114
1,1-Dichloropropene	26.3	25.7	28.0	26.7	3.7	133
cis-1,3-Dichloropropene	20.3	19.5	21.1	20.3	3.2	102
Ethylbenzene	24.7	24.5	25.5	24.9	1.7	125
Hexachlorobutadiene	23.0	25.3	25.2	24.5	4.3	123
Methylene chloride	26.0	25.7	26.1	25.9	0.7	130[a]
Naphthalene	13.8	12.7	11.8	12.8	6.4	63.8[a]
Styrene	24.2	23.3	23.3	23.6	1.8	118
1,1,1,2-Tetrachloroethane	21.4	20.2	21.3	21.0	2.6	105
1,1,2,2-Tetrachloroethane	18.6	17.8	19.0	18.5	2.7	92.3
Tetrachloroethene	25.2	24.8	26.4	25.5	2.7	127
Toluene	28.6	27.9	30.9	29.1	4.4	146[a]
1,2,4-Trichlorobenzene	15.0	14.4	12.9	14.1	6.3	70.5
1,1,1-Trichloroethane	28.1	27.2	29.9	28.4	4.0	142
1,1,2-Trichloroethane	20.8	19.6	21.7	20.7	4.2	104

TABLE 30 (cont.)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Trichloroethene	26.3	24.9	26.8	26.0	3.1	130
Trichlorofluoromethane	25.9	24.8	26.5	25.7	2.7	129
1,2,3-Trichloropropane	18.8	18.3	19.3	18.8	2.2	94.0
Vinyl chloride	24.8	23.2	23.9	24.0	2.7	120
m-Xylene/p-Xylene	24.3	23.9	25.3	24.5	2.4	123
o-Xylene	23.1	22.3	23.4	22.9	2.0	115

[a] Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

Compound	Detection Limit (ng)	Boiling Point (°C)
Chloromethane	58	-24
Bromomethane	26	4
Vinyl chloride	14	-13
Chloroethane	21	13
Methylene chloride	9	40
Acetone	35	56
Carbon disulfide	11	46
1,1-Dichloroethene	14	32
1,1-Dichloroethane	12	57
trans-1,2-Dichloroethene	11	48
Chloroform	11	62
1,2-Dichloroethane	13	83
1,1,1-Trichloroethane	8	74
Carbon tetrachloride	8	77
Bromodichloromethane	11	88
1,1,2,2-Tetrachloroethane**	23	146
1,2-Dichloropropane	12	95
trans-1,3-Dichloropropene	17	112
Trichloroethene	11	87
Dibromochloromethane	21	122
1,1,2-Trichloroethane	26	114
Benzene	26	80
cis-1,3-Dichloropropene	27	112
Bromoform**	26	150
Tetrachloroethene	11	121
Toluene	15	111
Chlorobenzene	15	132
Ethylbenzene**	21	136
Styrene**	46	145
Trichlorofluoromethane	17	24
Iodomethane	9	43
Acrylonitrile	13	78
Dibromomethane	14	97
1,2,3-Trichloropropane**	37	157
total Xylenes**	22	138-144

Footnotes are found on the following page.

TABLE 31 (cont.)

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* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrylonitrile	Bromodichloromethane
Bromomethane	Bromoform
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	Dibromomethane
Chloromethane	1,2-Dichloropropane
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane	trans-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	1,1,1-Trichloroethane
1,1-Dichloroethene	1,1,2-Trichloroethane
Trichloroethene	
trans-1,2-Dichloroethene	
Iodomethane	
Methylene chloride	
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylenes

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Detection Limit[a] (ppm)
Dichlorodifluoromethane	-30	Gas	0.20
Vinyl chloride	-19	Gas	0.11
1,3-Butadiene	-4	Gas	0.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane	4	Gas	0.14
Methyl bromide	4	Gas	0.14
Trichlorofluoromethane	24	88	0.18
1,1-Dichloroethene	31	22	0.07
Methylene chloride	40	44	0.05
1,1,2-Trichloro-trifluoroethane	48	37	0.13
Chloroform	61	21	0.04
1,1,1-Trichloroethane	75	13	0.03
Carbon tetrachloride	77	11	0.03
Benzene	80	10	0.16
Trichloroethene	87	8	0.04
1,2-Dichloropropane	96	5	0.05
Toluene	111	3	0.08
Tetrachloroethene	121	2	0.03

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

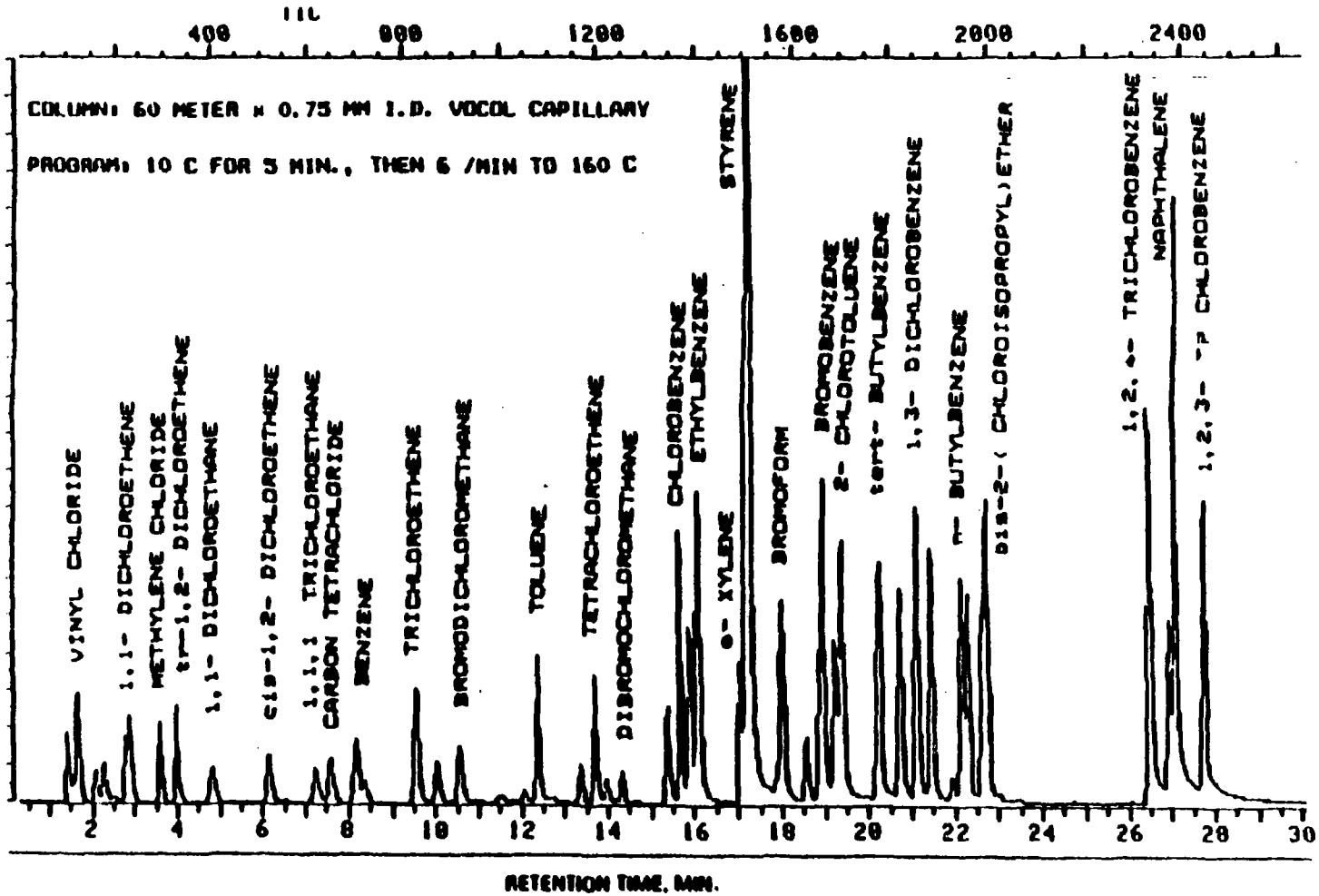


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

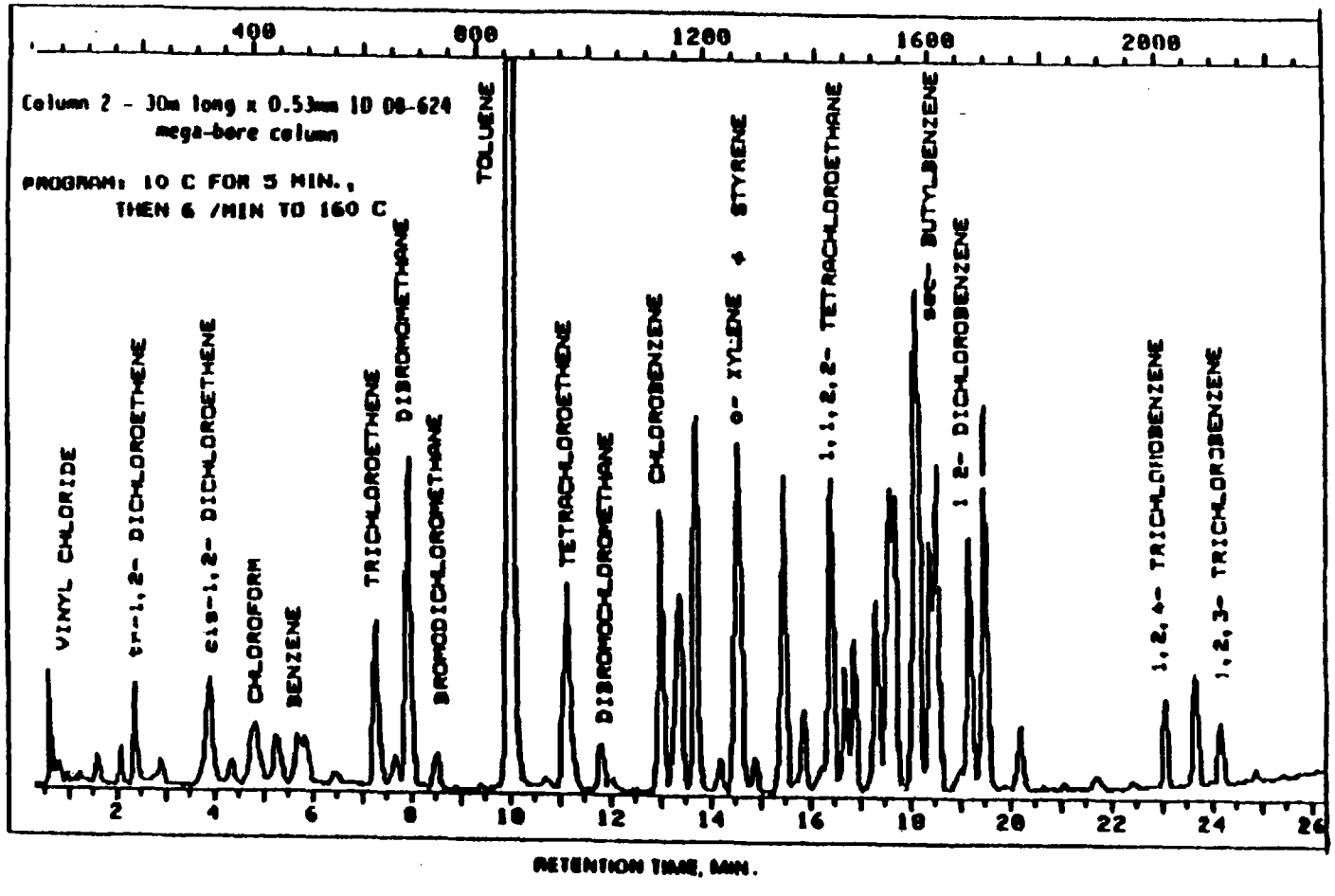


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

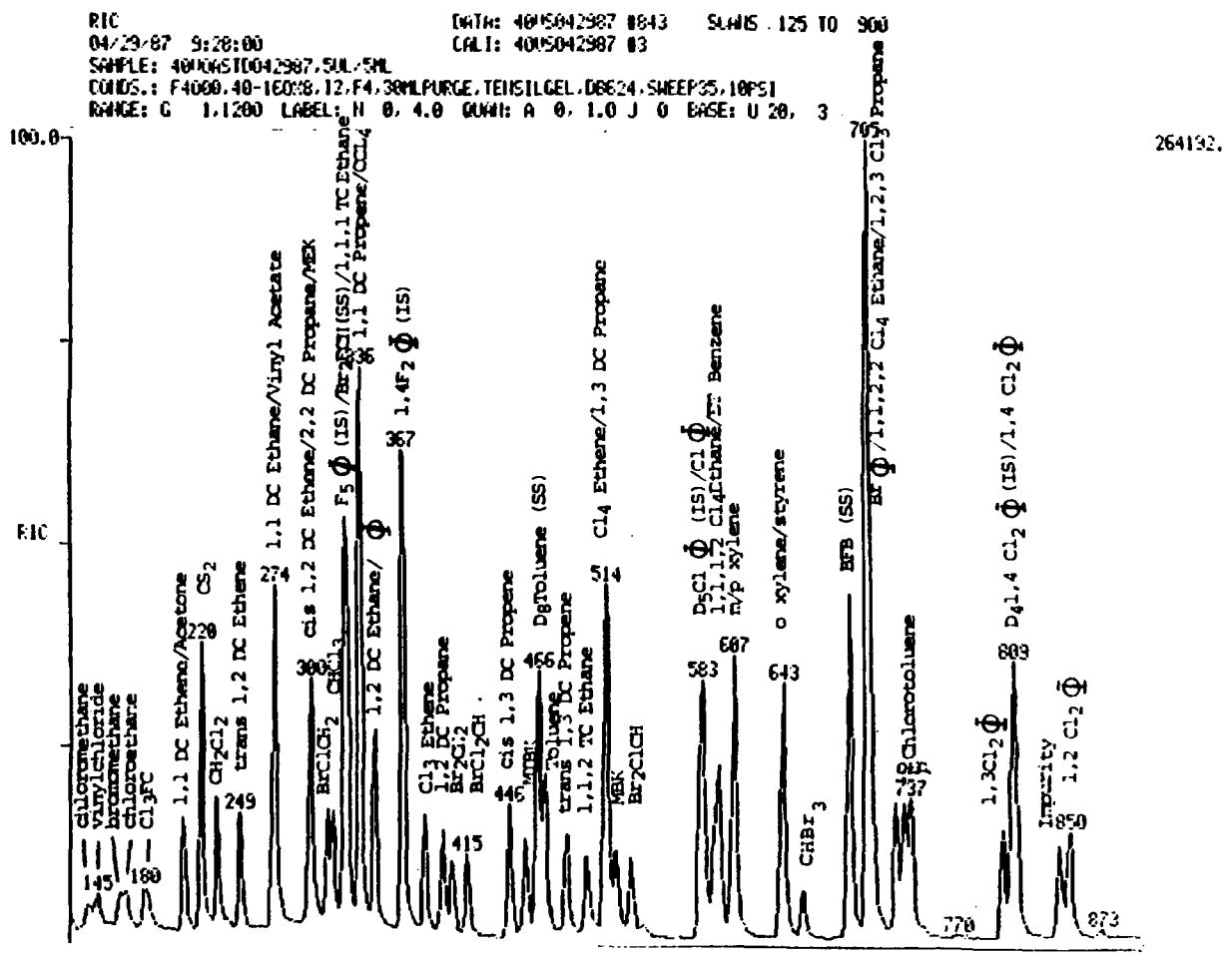
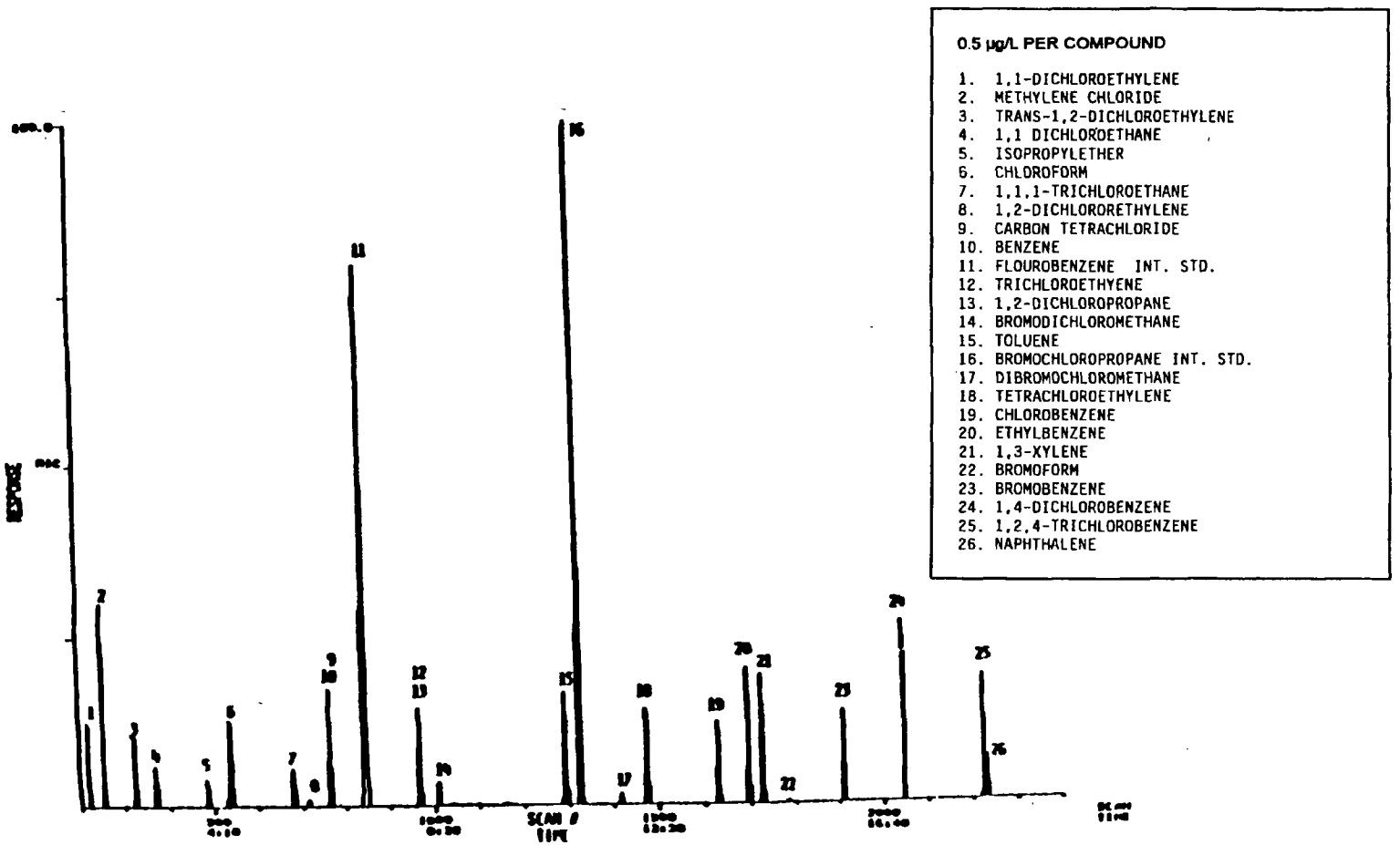
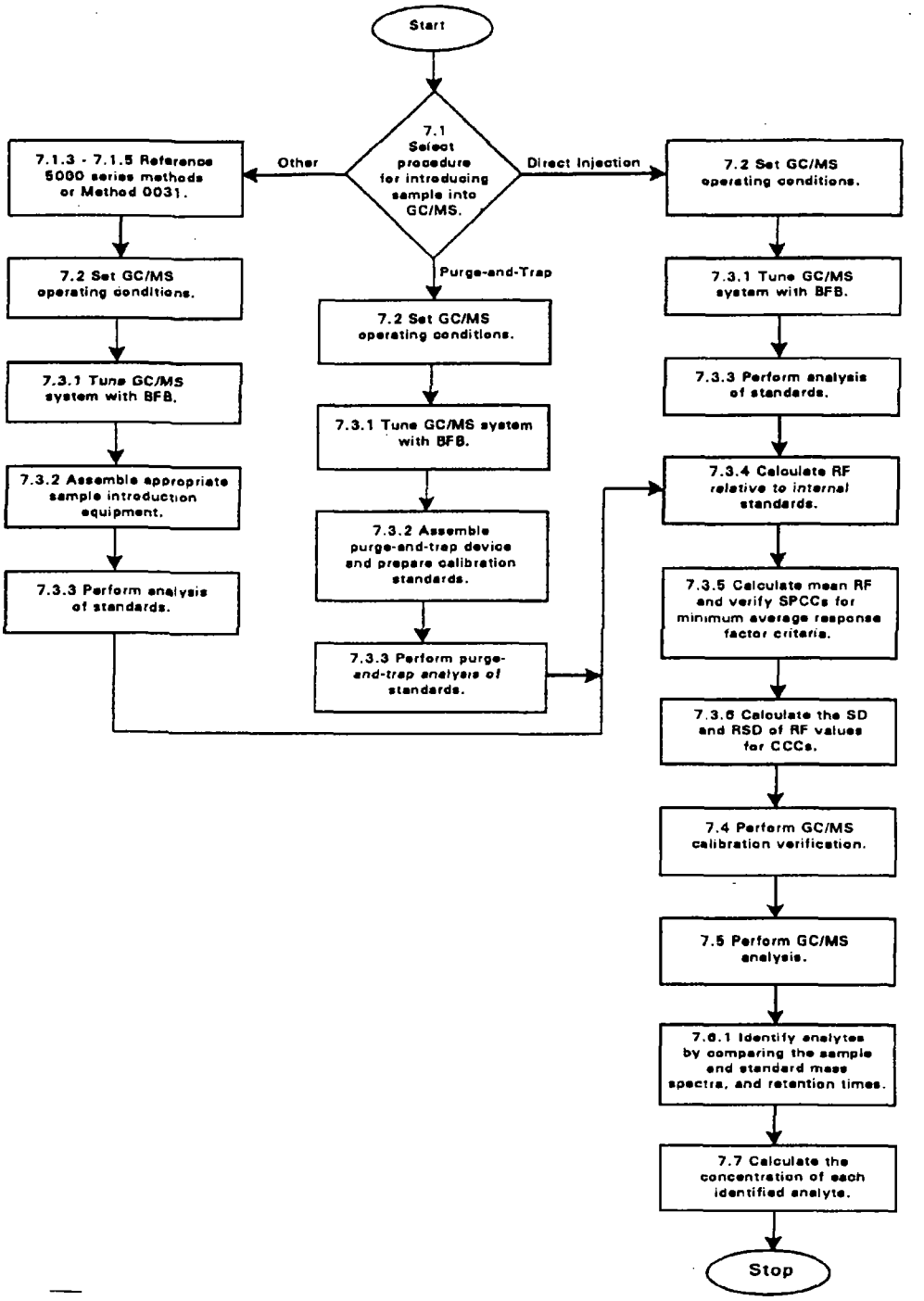


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Purge-and-Trap
Direct Injection
7.1.3 - 7.1.5 Reference 5000 series methods or Method 0031.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.5 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-15

Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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January 1999

Method TO-15
Acknowledgements

This Method was prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b), which was prepared under Contract No. 68-C3-0315, WA No. 3-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, and Scott Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development, were responsible for overseeing the preparation of this method. Additional support was provided by other members of the Compendia Workgroup, which include:

- John O. Burckle, EPA, ORD, Cincinnati, OH
- James L. Cheney, Corps of Engineers, Omaha, NB
- Michael Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
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This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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- Bill Taylor, Graseby, Smyrna, GA
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Finally, recognition is given to Frances Beyer, Lynn Kaufman, Debbie Bond, Cathy Whitaker, and Kathy Johnson of Midwest Research Institute's Administrative Services staff whose dedication and persistence during the development of this manuscript has enabled it's production.

DISCLAIMER

METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2).*

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how

to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

1.5 Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

1.6 Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings. The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

2. Summary of Method

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by

reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.5 The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3. Significance

3.1 Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see Appendix A) for water management thereby addressing a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.
- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management as noted in Appendix A of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., autoGCs and solid

adsorbents) that are often used. This method lists performance criteria that these alternatives must meet to be acceptable alternatives for monitoring ambient VOCs.

- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

3.2 With these features, Compendium Method TO-15 is a more general yet better defined method for VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

4. Applicable Documents

4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis.*
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures.*
- **Method E355** *Practice for Gas Chromatography Terms and Relationships.*
- **Method D5466** *Standard Test Method of Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology).*

4.2 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.
- *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June 1990.
- *Clean Air Act Amendments of 1990,* U. S. Congress, Washington, D.C., November 1990.

5. Definitions

[Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given below, all pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Gauge Pressure—pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

5.2 Absolute Pressure—pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

5.3 Cryogen—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp -195.8°C), liquid argon (bp -185.7°C), and liquid CO_2 (bp -79.5°C).

5.4 Dynamic Calibration—calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

5.5 Dynamic Dilution—means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

5.6 MS-SCAN—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

5.7 MS-SIM—mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

5.8 Qualitative Accuracy—the degree of measurement accuracy required to correctly identify compounds with an analytical system.

5.9 Quantitative Accuracy—the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

5.10 Replicate Precision—precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 11 for performance criteria for replicate precision).

5.11 Duplicate Precision—precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

5.12 Audit Accuracy—the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage (see Section 11 for performance criteria for audit accuracy).

6. Interferences and Contamination

6.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

6.2 Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

6.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

6.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

6.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

6.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

6.2.5 In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts).

7. Apparatus and Reagents

[Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus which may be of help in identifying options. The listings below are generic.]

7.1 Sampling Apparatus

[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Monitoring Program (UATMP), the non-methane organic compound (NMOC) sampling and analysis program, and the Photochemical Assessment Monitoring Stations (PAMS).]

7.1.1 Subatmospheric Pressure (see Figure 1, without metal bellows type pump).

7.1.1.1 Sampling Inlet Line. Stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample Canister. Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known manufacturers/resellers of canisters).

7.1.1.3 Stainless Steel Vacuum/Pressure Gauges. Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

7.1.1.4 Electronic Mass Flow Controller. Capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

7.1.1.5 Particulate Matter Filter. 2-μm sintered stainless steel in-line filter.

7.1.1.6 Electronic Timer. For unattended sample collection.

7.1.1.7 Solenoid Valve. Electrically-operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

7.1.1.9 Thermostatically Controlled Heater. To maintain above ambient temperature inside insulated sampler enclosure.

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

7.1.1.13 Maximum-Minimum Thermometer. Records highest and lowest temperatures during sampling period.

7.1.1.14 Stainless Steel Shut-off Valve. Leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary Vacuum Pump. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

[Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).

7.1.2.1 Sample Pump. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

[Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon 97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensation flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet.]

7.1.2.2 Other Supporting Materials. All other components of the pressurized sampling system are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

7.2 Analytical Apparatus

7.2.1 Sampling/Concentrator System (many commercial alternatives are available).

7.2.1.1 Electronic Mass Flow Controllers. Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

7.2.1.2 Vacuum Pump. General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings. Coated with fused silica to minimize active adsorption sites.

7.2.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

7.2.1.5 Gas Purifiers. Used to remove organic impurities and moisture from gas streams.

7.2.1.6 Six-port Gas Chromatographic Valve. For routing sample and carrier gas flows.

7.2.1.7 Multisorbent Concentrator. Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series.

7.2.1.7.1A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carbopack B (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) has been found to retain VOCs and allow some water vapor to pass through (6). The addition of a dry purging step allows for further water removal from the adsorbent trap. The steps constituting the dry purge technique that are normally used with multisorbent traps are illustrated in Figure 4. The optimum trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320 mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C. The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

7.2.1.7.2 An example of the effectiveness of dry purging is shown in Figure 5. The multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of the initial water content in the sample remains after sampling 500 mL of air. The detector response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted versus purge gas volume. Additional water reduction by a factor of 8 is indicated at temperatures of 45°C or higher. Still further water reduction is possible using a two-stage concentration/dryer system.

7.2.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.

7.2.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

7.2.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in Section 11.

7.2.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

7.2.2.3.1Linear Quadrupole Technology. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the

parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

7.2.2.3.2Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

7.2.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

7.2.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

7.2.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

7.3 Calibration System and Manifold Apparatus (see Figure 8)

7.3.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g.,1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

7.3.2 Humidifier. 500-mL impinger flask containing HPLC grade deionized water.

7.3.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

7.3.4 Teflon Filter(s). 47-mm Teflon® filter for particulate collection.

7.4 Reagents

7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 9).

7.4.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide. Used to cool secondary trap.

7.4.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

8. Collection of Samples in Canisters

8.1 Introduction

8.1.1 Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

8.1.2 Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

8.1.3 EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

8.2 Sampling System Description

8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].

8.2.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted-average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

8.2.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].

8.2.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

8.2.2.2 In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

8.2.3 All Samplers.

8.2.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate, mL/min.

P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister, mL.

T = sample period, hours.

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3 \text{ mL/min}$$

8.2.3.2 For automatic operation, the timer is designed to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

8.2.3.3 The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 2(b).

8.2.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.

8.2.3.5 As an option, a second electronic timer may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

8.2.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 8.4.1).

8.3 Sampling Procedure

8.3.1 The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

8.3.2 A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned according to the procedure outlined in Sections 8.4.2 and 8.4.4.

[Note: The sampling system should be contained in an appropriate enclosure.]

8.3.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

8.3.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as documented in Figure 9.

[Note: The following discussion is related to Figure 1]

8.3.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

[Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ±10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

[Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

8.3.6 The sampler is turned off and the elapsed time meter is reset to 000.0.

[Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]

8.3.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 8.4.1) canister is attached to the system.

8.3.8 The canister valve and vacuum/pressure gauge valve are opened.

8.3.9 Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated by the sampler vacuum/pressure gauge.

8.3.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister FTDS.

8.3.11 The electronic timer is set to start and stop the sampling period at the appropriate times. Sampling starts and stops by the programmed electronic timer.

8.3.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the FTDS. The current reading from the flow controller is recorded.

8.3.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the FTDS. Pressure should be close to desired pressure.

[Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.]

Time of day and elapsed time meter readings are also recorded.

8.3.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister FTDS (see Figure 9).

[Note: For a pressurized system, the final flow may be measured directly.]

The sampler is turned off.

8.3.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back to the analytical laboratory with other canisters in a canister shipping case.

8.4 Cleaning and Certification Program

8.4.1 Canister Cleaning and Certification.

8.4.1.1 All canisters must be clean and free of any contaminants before sample collection.

8.4.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

[Note: The canister cleaning system in Figure 10 can be used for this task.]

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.4.1.3 A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

[Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]

Air released/evacuated from canisters should be diverted to a fume hood.

8.4.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

8.4.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

8.4.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

8.4.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (see Appendix B) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

8.4.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

[Note: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed].

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

8.4.2 Cleaning Sampling System Components.

8.4.2.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

8.4.2.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

8.4.2.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

8.4.3 Zero Air Certification.

[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.]

8.4.3.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

8.4.3.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

8.4.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocussed on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocussed prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

8.4.4.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

8.4.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

8.4.4.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

8.4.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.4.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(b).

8.4.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.4.4.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

8.4.4.8 At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

8.4.4.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

8.4.5.1 Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

8.4.5.2 Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

9.1.1 The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. Two examples of concentrating systems are discussed. Other approaches are acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

9.1.2 With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

9.1.3 Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

9.1.4 With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

9.2 Preparation of Standards

9.2.1 Introduction.

9.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer's certificates of analysis must be retained to track the expiration date.

9.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

9.2.2 Preparing Working Standards.

9.2.2.1 Instrument Performance Check Standard. Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

9.2.2.2 Calibration Standards. Prepare five working calibration standards in humidified zero air at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each component under the optimized concentration parameters.

9.2.2.3 Internal Standard Spiking Mixture. Prepare an internal spiking mixture containing bromochloromethane, chlorobenzene-d_5, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

9.2.3 Standard Preparation by Dynamic Dilution Technique.

9.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

9.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.})\ (\text{Std. Gas Flowrate})}{(\text{Air Flowrate}) + (\text{Std. Gas Flowrate})}$$

9.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10\ \text{ppm})(1\ \text{mL/min})(1000\ \text{ppb/1 ppm})}{(1000\ \text{mL/min}) + (1\ \text{mL/min})} = 10\ \text{ppb}$$

9.2.4 Standard Preparation by Static Dilution Bottle Technique

[Note: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]

9.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

9.2.4.2 The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

9.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

9.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

9.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

9.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

9.2.4.7 The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where: V_a = Volume of liquid neat standard injected into the flask, µL.
d = Density of the liquid neat standard, mg/µL.
V_f = Volume of the flask, L.

9.2.4.8 To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

[Note: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).]

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]

9.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

9.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

9.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

9.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

[Note: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]

9.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

9.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = \frac{\text{Volume}_{\text{standard}}}{\text{Volume}_{\text{dilution gas}}} \times 10^9$$

[Note: Both values must be expressed in the same units.]

9.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equations:

$$V = \frac{nRT}{P}$$

and:

$$n = \frac{(mL)(d)}{MW}$$

where:
- V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.
- n = Moles.
- R = Gas constant, 0.08206 L-atm/mole °K.
- T = 298°K (standard temperature).
- P = 1 standard pressure, 760 mm Hg (1 atm).
- mL = Volume of liquid injected, mL.
- d = Density of the neat standard, g/mL.
- MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppb units.

9.2.6 Standard Preparation by Water Methods.

[Note: Standards may be prepared by a water purge and trap method (14) and summarized as follows].

9.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

9.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

[Note: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.]

9.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

9.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

9.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

9.2.6.6 The canister is allowed to equilibrate overnight before use.

9.2.6.7 A schematic of this approach is shown in Figure 14.

9.2.7 Preparation of Standards by Permeation Tubes.

9.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

9.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

9.2.8 Storage of Standards.

9.2.8.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

9.2.8.2 It is imperative that a storage logbook be kept to document storage time.

10. GC/MS Operating Conditions

10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

10.1.1 Sample Collection Conditions

Cryogenic Trap	Adsorbent Trap

Set point	-150°C	Set point	27°C
Sample volume	- up to 100 mL	Sample volume	- up to 1,000 mL
Carrier gas purge flow	- none	Carrier gas purge flow	- selectable

[Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. Other preconcentration systems may be used provided performance standards (see Section 11) are realized.]

10.1.2 Desorption Conditions

Cryogenic Trap		Adsorbent Trap	
Desorb Temperature	120°C	Desorb Temperature	Variable
Desorb Flow Rate	~ 3 mL/min He	Desorb Flow Rate	~3 mL/min He
Desorb Time	<60 sec	Desorb Time	<60 sec

The adsorbent trap conditions depend on the specific solid adsorbents chosen (see manufacturers' specifications).

10.1.3 Trap Reconditioning Conditions.

Cryogenic Trap		Adsorbent Trap	
Initial bakeout	120°C (24 hrs)	Initial bakeout	
Variable (24 hrs)			
After each run	120°C (5 min)	After each run	Variable (5 min)

10.2 GC/MS System

10.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

10.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 μm film thickness fused silica column with refocusing on the column.

Item	Condition	
Carrier Gas:	Helium	
Flow Rate:	Generally 1-3 mL/min as recommended by manufacturer	
Temperature Program:	Initial Temperature:	-50°C
	Initial Hold Time:	2 min
	Ramp Rate:	8° C/min
	Final Temperature:	200°C
	Final Hold Time:	Until all target compounds elute.

10.2.3 The following are the recommended mass spectrometer conditions:

Item	Condition

Electron Energy:	70 Volts (nominal)
Mass Range:	35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here.
Scan Time:	To give at least 10 scans per peak, not to exceed 1 second per scan].

A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

10.3 Analytical Sequence

10.3.1 Introduction. The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.
- Perform a laboratory method blank.
- Complete this sequence for analysis of ≤20 field samples.

10.4 Instrument Performance Check

10.4.1 Summary. It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

10.4.2 Frequency. Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation.

The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

10.4.3 Procedure. The analysis of the instrument performance check standard is performed by trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

10.4.4 Technical Acceptance Criteria. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

10.4.5 Corrective Action. If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

10.4.6 Documentation. Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

10.5 Initial Calibration

10.5.1 Summary. Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

10.5.2 Frequency. Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed.

If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

10.5.3 Procedure. Verify that the GC/MS system meets the instrument performance criteria in Section 10.4.

The GC must be operated using temperature and flow rate parameters equivalent to those in Section 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 9.2 or equivalent.

A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 10.5.1 and 10.5.5.

Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

10.5.4 Calculations.

[Note: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.]

10.5.4.1 Relative Response Factor (RRF). Calculate the relative response factors for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

where: RRF = Relative response factor.
A_x = Area of the primary ion for the compound to be measured, counts.
A_{is} = Area of the primary ion for the internal standard, counts.
C_{is} = Concentration of internal standard spiking mixture, ppbv.
C_x = Concentration of the compound in the calibration standard, ppbv.

[Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. C_{is} and C_x must be in the same units.]

10.5.4.2 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{x_i}{n}$$

where: $\overline{RRF}$ = Mean relative response factor.
x_i = RRF of the compound at concentration i.
n = Number of concentration values, in this case 5.

10.5.4.3 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

where: SD_{RRF} = Standard deviation of initial response factors (per compound).
RRF_i = Relative response factor at a concentration level i.
$\overline{RRF}$ = Mean of initial relative response factors (per compound).

10.5.4.4 Relative Retention Times (RRT). Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where: RT_c = Retention time of the target compound, seconds
RT_{is} = Retention time of the internal standard, seconds.

10.5.4.5 Mean of the Relative Retention Times ($\overline{RRT}$). Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

where: $\overline{RRT}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

10.5.4.6 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

10.5.4.7 Mean Area Response ($\overline{Y}$) for Internal Standard. Calculate the mean area response ($\overline{Y}$) for each internal standard compound over the initial calibration range using the following equation:

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

where: $\overline{Y}$ = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

10.5.4.8 Mean Retention Times ($\overline{RT}$). Calculate the mean of the retention times ($\overline{RT}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where: $\overline{RT}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

10.5.5.1 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

[Note: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.]

10.5.5.2 The RRT for each target compound at each calibration level must be withiin 0.06 RRT units of the mean RRT for the compound.

10.5.5.3 The area response Y of at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range for each internal standard.

10.5.5.4 The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.5.6 Corrective Action.

10.5.6.1 Criteria. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

10.5.6.2 Schedule. Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

10.6 Daily Calibration

10.6.1 Summary. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

10.6.2 Frequency. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

10.6.3 Procedure. The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

10.6.4 Calculations. Perform the following calculations.

[Note: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.]

10.6.4.1 Relative Response Factor (RRF). Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

10.6.4.2 Percent Difference (%D). Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where: RRF_c = RRF of the compound in the continuing calibration standard.

$\overline{RRF_i}$ = Mean RRF of the compound in the most recent initial calibration.

10.6.5 Technical Acceptance Criteria. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

10.6.6 Corrective Action. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

10.7 Blank Analyses

10.7.1 Summary. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank

using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

10.7.2 Frequency. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

10.7.3 Procedure. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

10.7.4 Calculations. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

10.7.5 Technical Acceptance Criteria. A blank canister should be analyzed daily.

The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration.

The retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL as defined in Section 11.2) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

10.7.6 Corrective Action. If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

10.8 Sample Analysis

10.8.1 Summary. An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

[Note: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary

in humidity, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.]

10.8.2 Frequency. If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard.

If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.8.3 Procedure for Instrumental Analysis. Perform the following procedure for analysis.

10.8.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.8.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.8.3.3 Connect the sample canister to the inlet of the GC/MS analytical system, as shown in Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.8.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.8.3.5 Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate method) introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.8.3.6 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.8.3.7 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.8.3.8 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.8.3.9 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

10.8.4 Calculations. The equation below is used for calculating concentrations.

$$C_x = \frac{A_x C_{is} DF}{A_{is} \overline{RRF}}$$

where: C_x = Compound concentration, ppbv.

A_x = Area of the characteristic ion for the compound to be measured, counts.

A_{is} = Area of the characteristic ion for the specific internal standard, counts.

C_{is} = Concentration of the internal standard spiking mixture, ppbv

$\overline{RRF}$ = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

[Note: The equation above is valid under the condition that the volume (~500 µL) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.]

10.8.5 Technical Acceptance Criteria.

[Note: If the most recent valid calibration is an initial calibration, internal standard area responses and RTs in the sample are evaluated against the corresponding internal standard area responses and RTs in the mid level standard (10 ppbv) of the initial calibration.]

10.8.5.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria at the frequency described in Sections 10.4, 10.5 and 10.6.

10.8.5.2 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

10.8.5.3 All of the target analyte peaks should be within the initial calibration range.

10.8.5.4 The retention time for each internal standard must be within ±0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

10.8.6 Corrective Action. If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

[Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.]

10.8.6.1 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

10.8.6.2 If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and

corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.8.6.3 If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

11.1 Introduction

11.1.1 There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

11.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria, and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

11.1.3 Specific criteria for each Title III compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

11.2 Method Detection Limit

11.2.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

11.2.2 The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

11.3 Replicate Precision

11.3.1 The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where:

x_1 = First measurement value.

x_2 = Second measurement value.

$\bar{x}$ = Average of the two values.

11.3.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data are summarized in Table 5 and suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

11.4 Audit Accuracy

11.4.1 A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\text{Audit Accuracy, \%} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

11.4.2 Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

12. References

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3. Coutant, R.W., *Theoretical Evaluation of Stability of Volatile Organic Chemicals and Polar Volatile Organic Chemicals in Canisters*, U. S. Environmental Protection Agency, EPA Contract No. 68-DO-0007, Work Assignment No. 45, Subtask 2, Battelle, Columbus, OH, June 1993.

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APPENDIX A.

LISTING OF SOME COMMERCIAL WATER MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio. 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 93065
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (FAX)
[Variable Temperature Adsorption Trap]

APPENDIX B.

COMMENT ON CANISTER CLEANING PROCEDURES

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

APPENDIX C.

LISTING OF COMMERCIAL MANUFACTURERS AND RE-SUPPLIERS OF SPECIALLY-PREPARED CANISTERS

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

APPENDIX D.

LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST--MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH3Cl	74-87-3	-23.7	3.8 x 10	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7 x 10	60.1		
Vinyl chloride (chloroethene); C2H3Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH2N2	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH2O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C4H6	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH3Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl2O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C2H3Br	593-60-2	15.8	1.1 x 10	107		
Ethylene oxide; C2H4O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C2H4O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	31.7	500	97	X	X
Propylene oxide; C3H6O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH3I	74-88-4	42.4	400	141.9		
Methylene chloride; CH2Cl2	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C2H3NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS2	75-15-0	46.5	260	76		
Methyl tert-butyl ether; C5H12O	1634-04-4	55.2	249	86		
Propionaldehyde; C2H5CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	57.0	230	99	X	

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C2H5ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C3H4O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	63.0	163	72		
Chloroform; CHCl3	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C2H5N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C2H8N2	57-14-7	63	157.0	60.0		
Hexane; C6H14	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C3H7N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C2H3Cl3	71-55-6	74.1	100	133.4	X	X
Methanol; CH4O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl4	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C4H6O2	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	79.6	77.5	72		X
Benzene; C6H6	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C2H3N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	83.5	61.5	99	X	X
Triethylamine; C6H15N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH6N2	60-34-4	87. 8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C8H18	540-84-1	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C4H8O2	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	104	30.0	115		
Ethyl acrylate; C5H8O2	140-88-5	100	29.3	100		
Methyl methacrylate; C5H8O2	80-62-6	101	28.0	100.1		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmgHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl methacrylate; C5H8O2	80-62-101	101	28.0	100.1		
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	112	27.8	111	X	X
Toluene; C7H8	108-88-3	111	22.0	92	X	X
Trichloroethylene; C2HCl3	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C2Cl4	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C2H5N3O2	684-93-5	124	10.0	103		
2-Nitropropane; C3H7NO2	79-46-9	120	10.0	89		
Chlorobenzene; C6H5Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C8H10	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C8H10	1330-20-7	142	6.7	106.2	X	X
Styrene; C8H8	100-42-5	145	6.6	104	X	X
p-Xylene; C8H10	106-42-3	138	6.5	106.2	X	X
m-Xylene; C8H10	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr3	75-25-2	149	5.6	252.8		
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	146	5.0	167.9	X	X
o-Xylene; C8H10	95-47-6	144	5.0	106.2	X	X
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C2H6N2O	62-75-9	152	3.7	74		
Beta-Propiolactone; C3H4O2	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C9H12	98-82-8	153	3.2	120		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Cumene (isopropylbenzene); C9H12	98-82-8	153	3.2	120		
Acrylic acid; C3H4O2	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C3H7NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C3H6O3S	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C8H8O	98-86-2	202	1.0	120		
Dimethyl sulfate; C2H6O4S	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	178	0.71	143		
Chloroacetic acid; C2H3ClO2	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C6H7N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C3H7NO2	51-79-6	183	0.54	89		
Acrylamide; C3H5NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C8H11N	121-69-7	192	0.50	121		
Hexachloroethane; C2Cl6	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C4Cl6	87-68-3	215	0.40	260.8	X	X
Isophorone; C9H14O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C4H8N2O2	59-89-2	225	0.32	116.1		
Styrene oxide; C8H8O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C4H10O4S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture);C7H8O	1319-77-3	202	0.26	108		
o-Cresol; C7H8O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	213	0.18	181.5	X	X
nitrobenzene C6H5NO2	98-95-3	211	0.15	123		

[1]Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:
(a)D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC. October 1992;
(b)R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and
(c)R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTIFYING THE TITLE III CLEAN AIR ACT AMENDMENT COMPOUNDS

Compound	CAS No.	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH3Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-S8-1	60	62
Vinyl chloride (chloroethene); C2H3Cl	7S-01-4	62	64
Diazomethane; CH2N2	334-88-3	42	41
Formaldehyde; CH2O	50-00-0	29	30
1,3-Butadiene; C4H6	106-99-0	39	54
Methyl bromide (bromomethane); CH3Br	74-83-9	94	96
Phosgene; CCl2O	75-44-5	63	65
Vinyl bromide (bromoethene); C2H3Br	593-60-2	106	108
Ethylene oxide; C2H4O	75-21-8	29	44
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	64	66
Acetaldehyde (ethanal); C2H4O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	61	96
Propylene oxide; C3H6O	75-56-9	58	57
Methyl iodide (iodomethane); CH3I	74-88-4	142	127
Methylene chloride; CH2Cl2	75-09-2	49	84, 86
Methyl isocyanate; C2H3NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	76	41, 78
Carbon disulfide; CS2	75-15-0	76	44, 78
Methyl tert-butyl ether; C5H12O	1634-04-4	73	41, 53
Propionaldehyde; C2H5CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C2H5ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C3H4O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	42	41, 72
Chloroform; CHCl3	67-66-3	83	85, 47
Ethyleneimine (aziridine); C2H5N	151-56-4	42	43
1,1-Dimethylhydrazine; C2H8N2	57-14-7	60	45, 59
Hexane; C6H14	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylazindine); C3H7N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); C2H3Cl3	71-55-6	97	99, 61
Methanol; CH4O	67-56-1	31	29
Carbon tetrachloride; CCl4	56-23-5	117	119
Vinyl acetate; C4H6O2	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	43	72

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Benzene; C6H6	71-43-2	78	77,50
Acetonitrile (cyanomethane); C2H3N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	62	64, 27
Triethylamine; C6H15N	121-44-8	86	58, 101
Methylhydrazine; CH6N2	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C8H18	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); C4H8O2	123-91-1	88	58
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	79	49, 81
Ethyl acrylate; C5H8O2	140-88-5	55	73
Methyl methacrylate; C5H8O2	80-62-6	41	69, 100
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	75	39, 77
Toluene; C7H8	108-88-3	91	92
Trichloethylene; C2HCl3	79-01-6	130	132, 95
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	97	83, 61
Tetrachloroethylene; C2Cl4	127-18-4	166	164, 131
Epichlorohydrin (l-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	107	109
N-Nitrso-N-methylurea; C2H5N3O2	684-93-5	60	44, 103
2-Nitropropane; C3H7NO2	79-46-9	43	41
Chlorobenzene; C6H5Cl	108-90-7	112	77, 114
Ethylbenzene; C8H10	100-41-4	91	106
Xylenes (isomer & mixtures); C8H10	1330-20-7	91	106
Styrene; C8H8	100-42-5	104	78, 103
p-Xylene; C8H10	106-42-3	91	106
m-Xylene; C8H10	108-38-3	91	106
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr3	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	83	85
o-Xylene; C8H10	95-47-6	91	106
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C2H6N2O	62-75-9	74	42
Beta-Propiolactone; C3H4O2	57-57-8	42	43
Cumene (isopropylbenzene); C9H12	98-82-8	105	120
Acrylic acid; C3H4O2	79-10-7	72	45, 55
N,N-Dimethylformamide; C3H7NO	68-12-2	73	42, 44
1,3-Propane sultone; C3H6O3S	1120-71-4	58	65, 122

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Acetophenone; C8H8O	98-86-2	105	77,120
Dimethyl sulfate; C2H6O4S	77-78-1	95	66,96
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	93	63, 95
Chloroacetic acid; C2H3ClO2	79-11-8	50	45, 60
Aniline (aminobenzene); C6H7N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	146	148, 111
Ethyl carbamate (urethane); C3H7NO2	51-79-6	31	44, 62
Acrylamide; C3H5NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C8H11N	121-69-7	120	77, 121
Hexachloroethane; C2Cl6	67-72-1	201	199, 203
Hexachlorobutadiene; C4Cl6	87-68-3	225	227, 223
Isophorone; C9H14O	78-59-1	82	138
N-Nitrosomorpholine; C4H8N2O2	59-89-2	56	86, 116
Styrene oxide; C8H8O	96-09-3	91	120
Diethyl sulfate; C4H10O4S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture); C7H8O	1319-77-3		
o-Cresol; C7H8O	95-48-7	108	107
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	110	64
Phenol; C6H6O	108-95-2	94	66
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	180	182, 184
Nitrobenzene; C6H5NO2	98-95-3	77	51, 123

TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 Percent of m/e 95
75	30.0 to 66.0 Percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95 (See note)
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

[1]All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4. METHOD DETECTION LIMITS (MDL)[1]

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride	–	–
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane	–	0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	–
1,1-Dichloroethane	0.27	0.05
1,2-Dichloroethane	0.24	–
1,1-Dichloroethene	–	0.22
cis-1,2-Dichloroethene	–	0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	–
cis-1,3-Dichloropropene	0.36	–
trans-1,3-Dichloropropene	0.22	–
Ethylbenzene	0.27	0.05
Chloroethane	0.19	–
Trichlorofluoromethane	–	–
1,1,2-Trichloro-1,2,2-trifluoroethane		–
1,2-Dichloro-1,1,2,2-tetrafluoroethane	–	–
Dichlorodifluoromethane	–	–
Hexachlorobutadiene	–	–
Bromomethane	0.53	–
Chloromethane	0.40	–
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene	–	–
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	–
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene	–	–
1,3,5-Trimethylbenzene	–	–
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28

[1]Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP) FROM EPA NETWORK OPERATIONS[1]

Monitoring Compound Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59[2]	1.1	8.7	47	0.2[2]
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--

[1]Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.
[2]Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

TABLE 6. AUDIT ACCURACY (AA) VALUES[1] FOR SELECTED COMPENDIUM METHOD TO-14A COMPOUNDS

Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2

[1]Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.

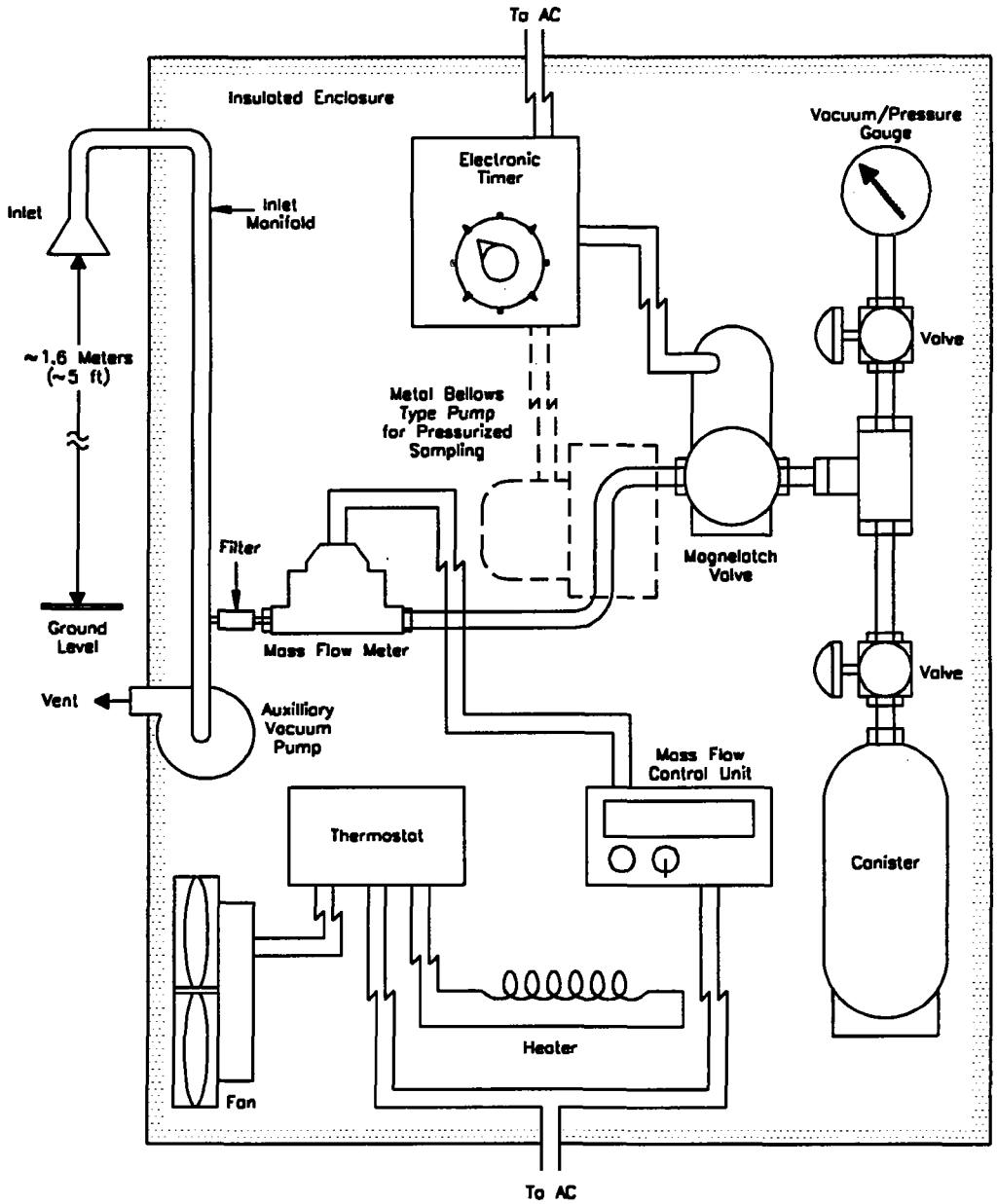
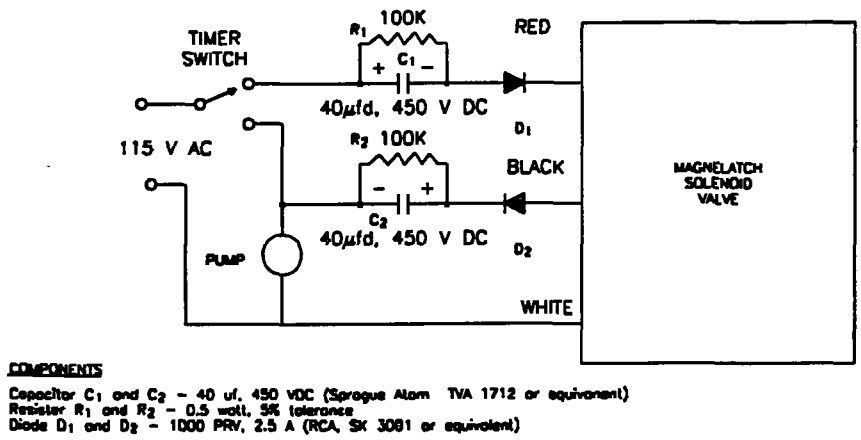
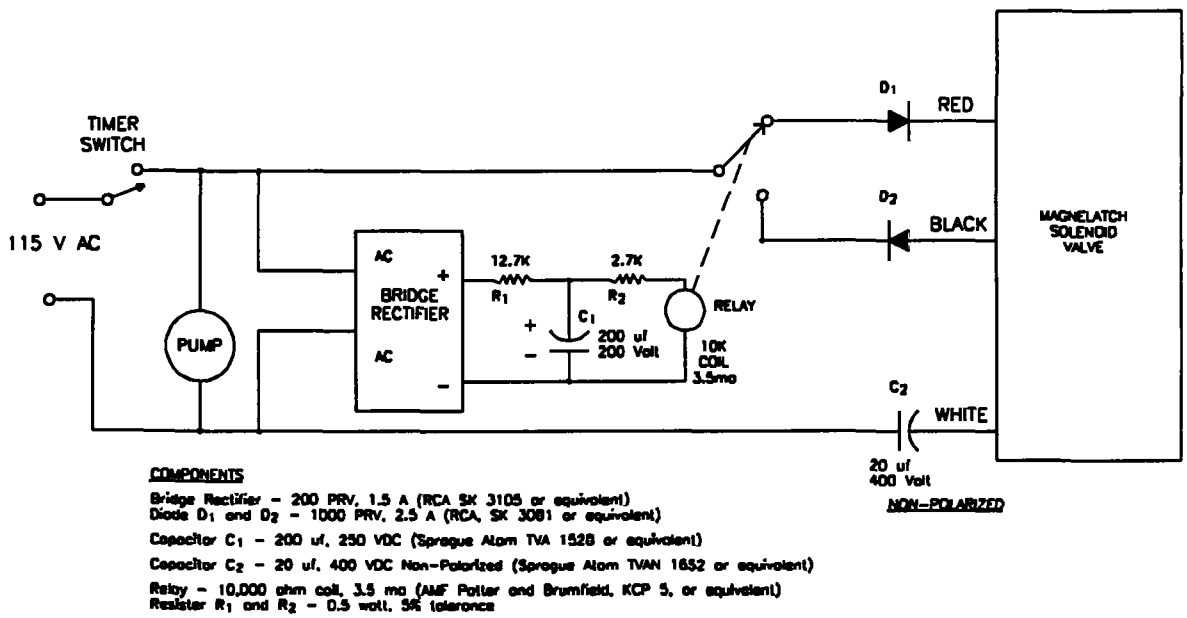


Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.



(a). Simple Circuit for Operating Magnelatch Valve



(b). Improved Circuit Designed to Handle Power Interruptions

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.

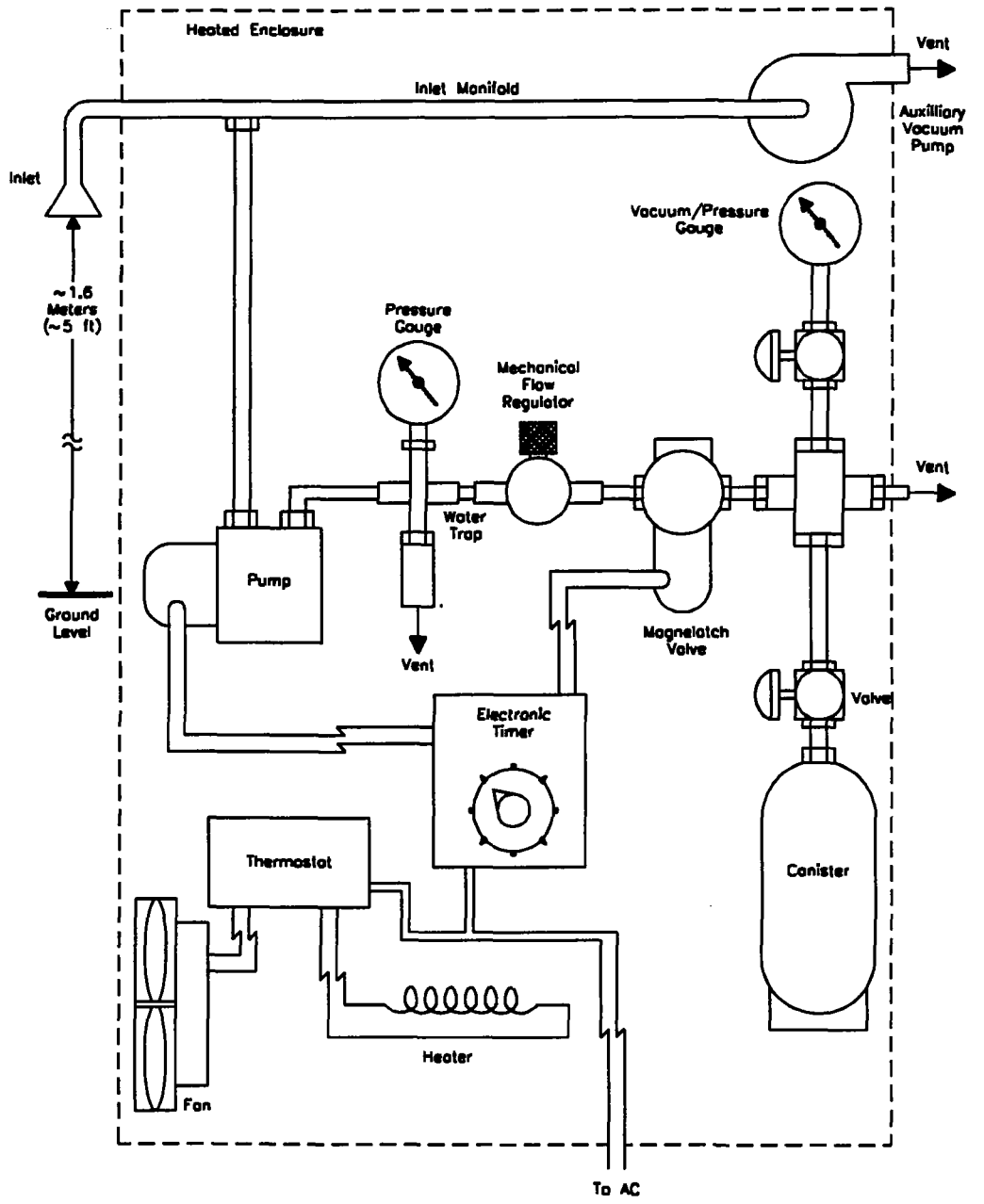


Figure 3. Alternative sampler configuration for pressurized canister sampling.

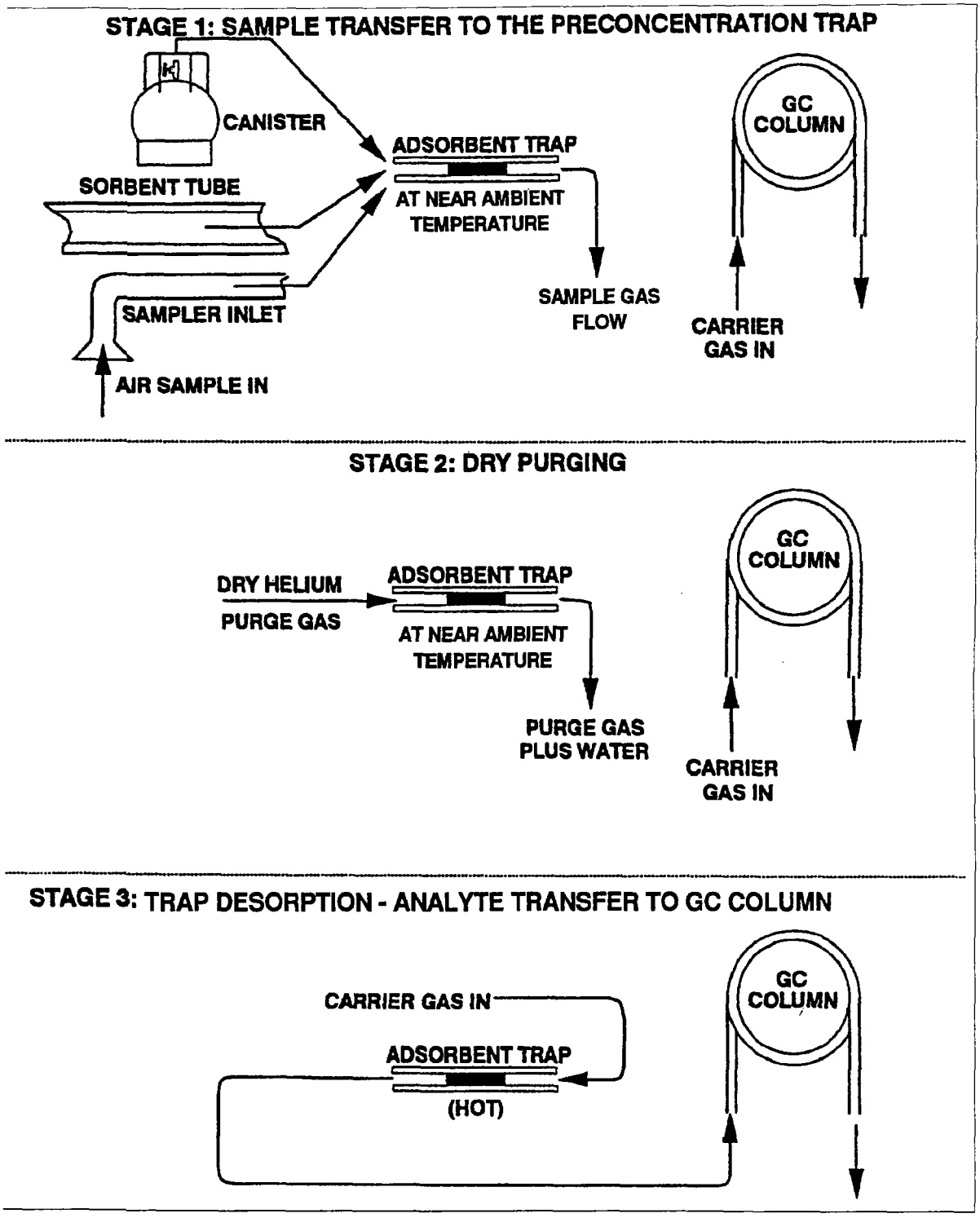


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

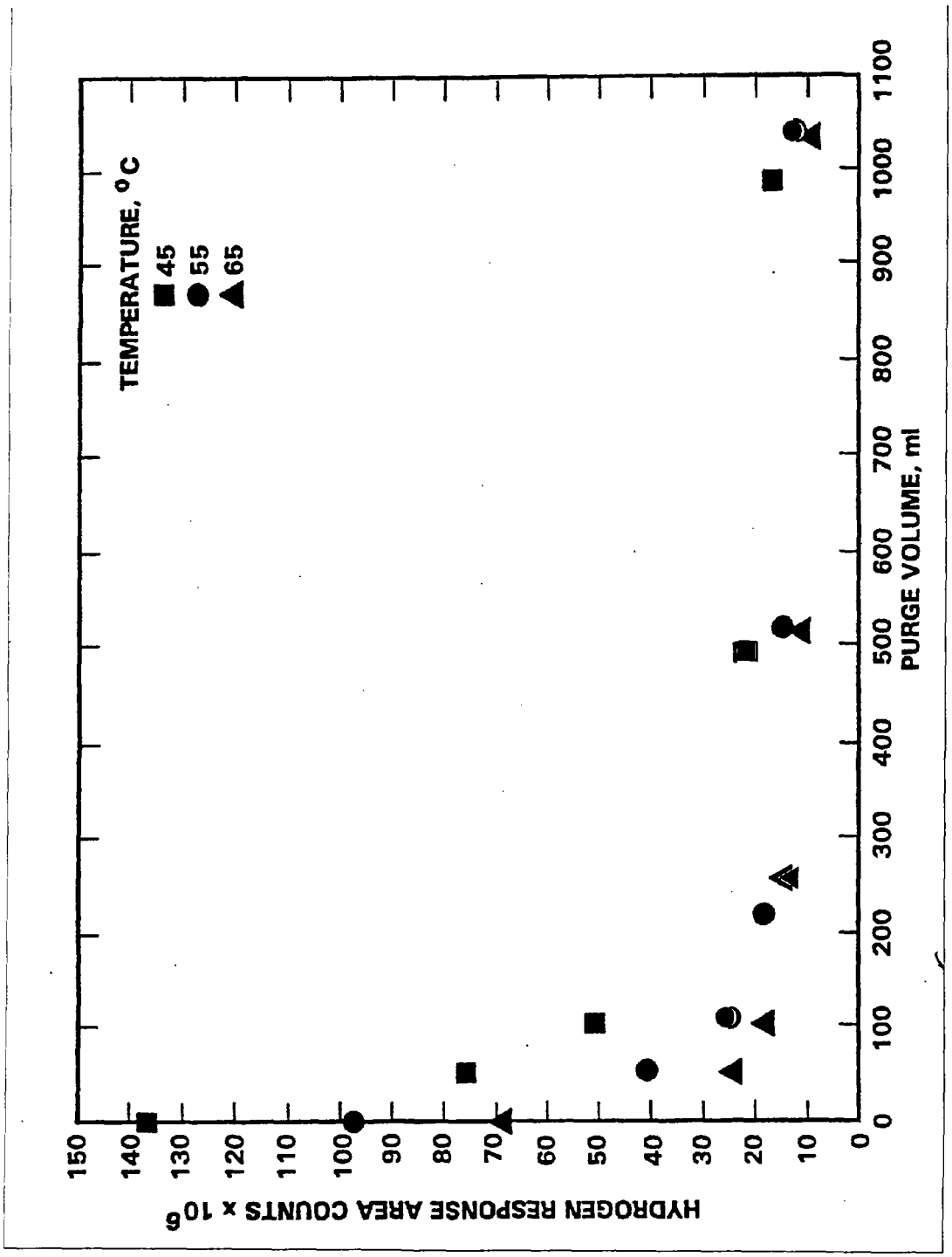


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

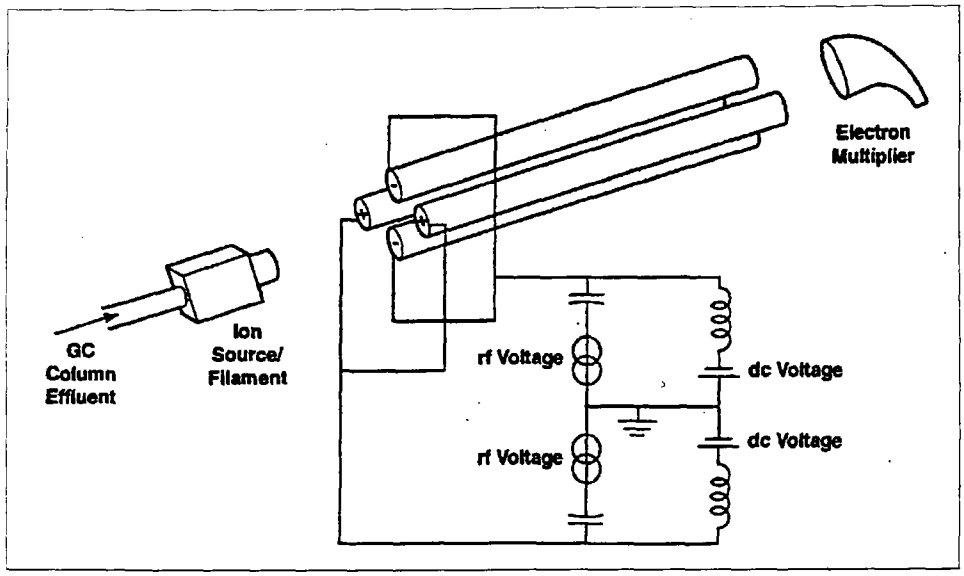


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

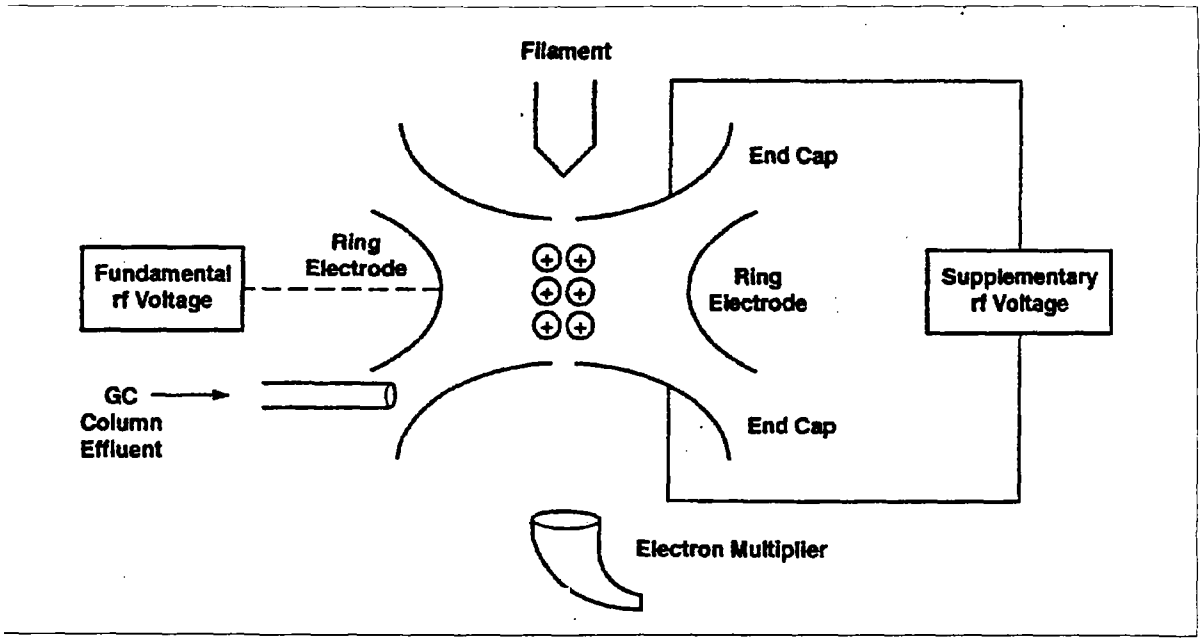


Figure 7. Simplified diagram of an ion trap mass spectrometer.

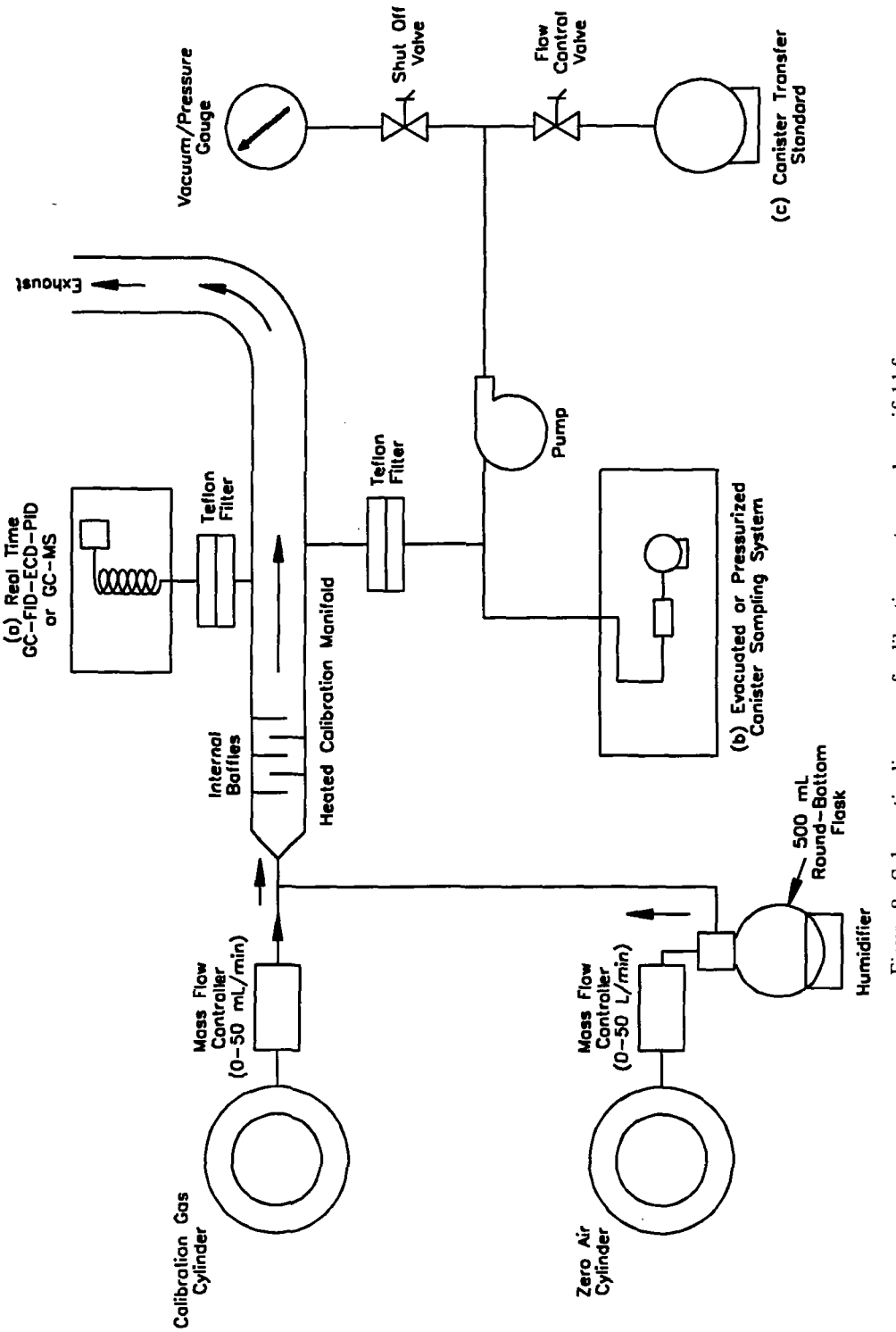


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET

A.GENERAL INFORMATION

SITE LOCATION: _____
SITE ADDRESS: _____
_____
SAMPLING DATE: _____

SHIPPING DATE: _____
CANISTER SERIAL NO.: _____
SAMPLER ID: _____
OPERATOR: _____
CANISTER LEAK
CHECK DATE: _____

B. SAMPLING INFORMATION

	TEMPERATURE				PRESSURE	
	INTERIOR	AMBIENT	MAXIMUM	MINIMUM	CANISTER PRESSURE	
START						
STOP						

	SAMPLING TIMES		FLOW RATES		
	LOCAL TIME	ELAPSED TIME METER READING	MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT
START					
STOP					

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATA RECEIVED: _____
RECEIVED BY: _____
INITIAL PRESSURE: _____
FINAL PRESSURE: _____
DILUTION FACTOR: _____
ANALYSIS
GC-FID-ECD DATE: _____
GC-MSD-SCAN DATE: _____
GC-MSD-SIM DATE: _____
RESULTS*: _____
_____
GC-FID-ECD: _____
GC-MSD-SCAN: _____
GC-MSD-SIM: _____

_____
SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).

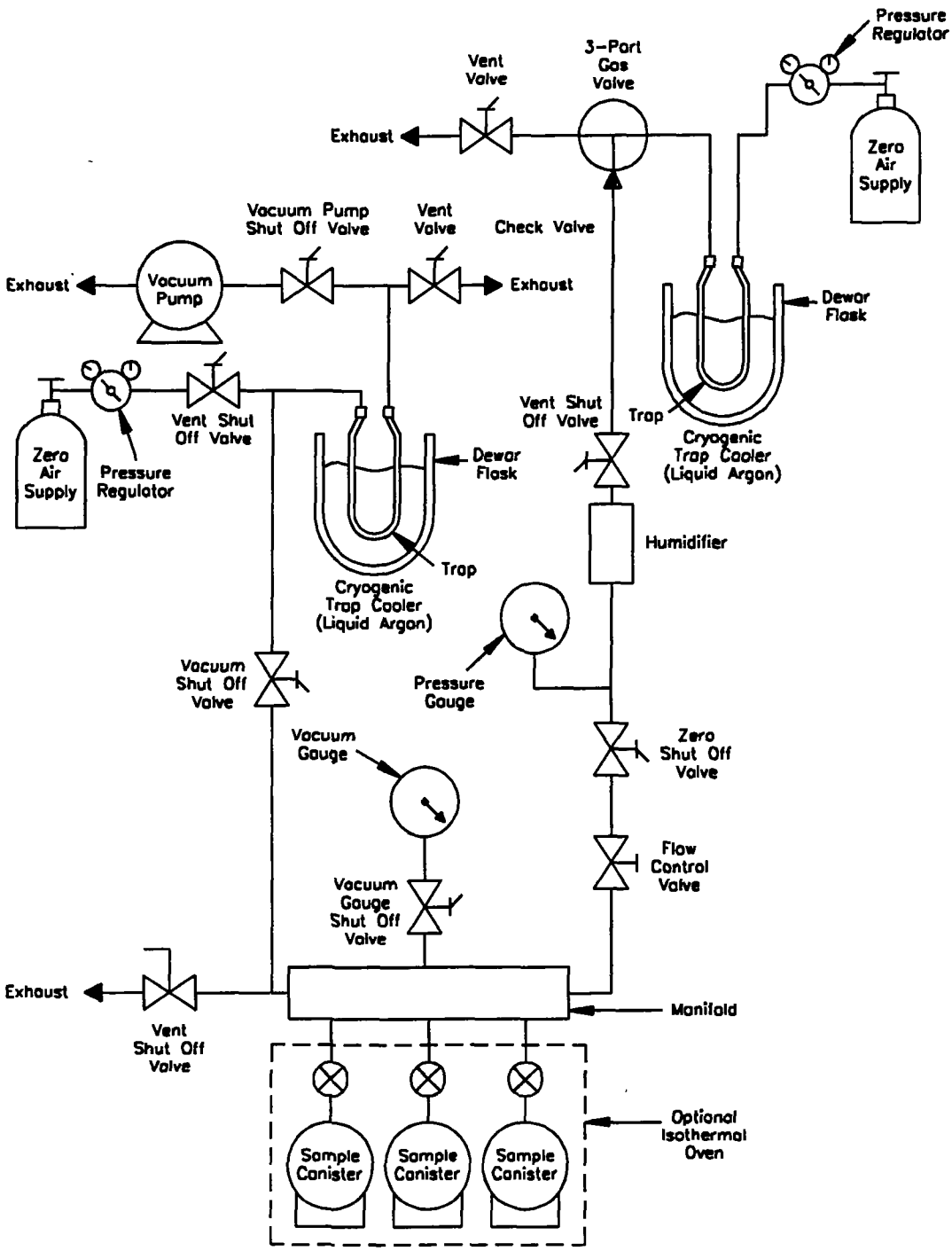


Figure 10. Canister cleaning system.

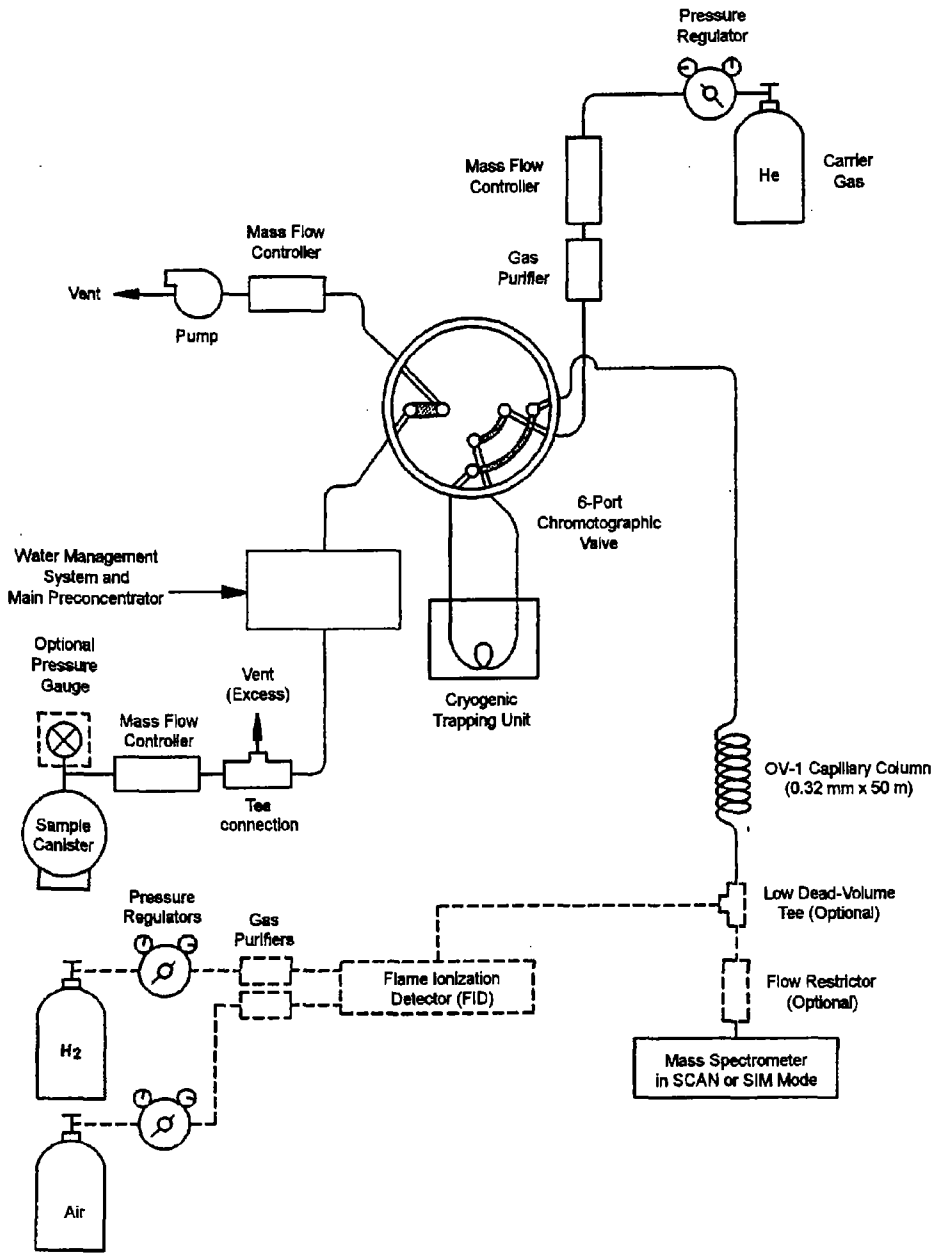
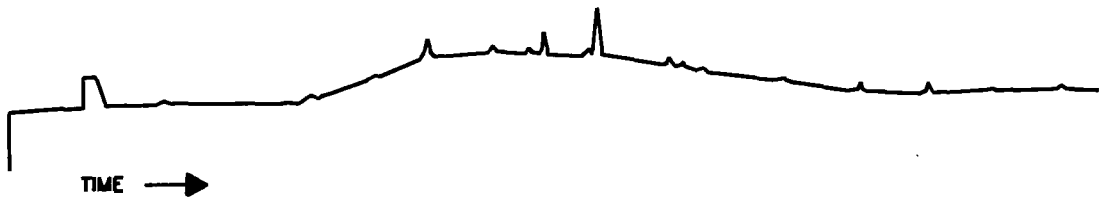
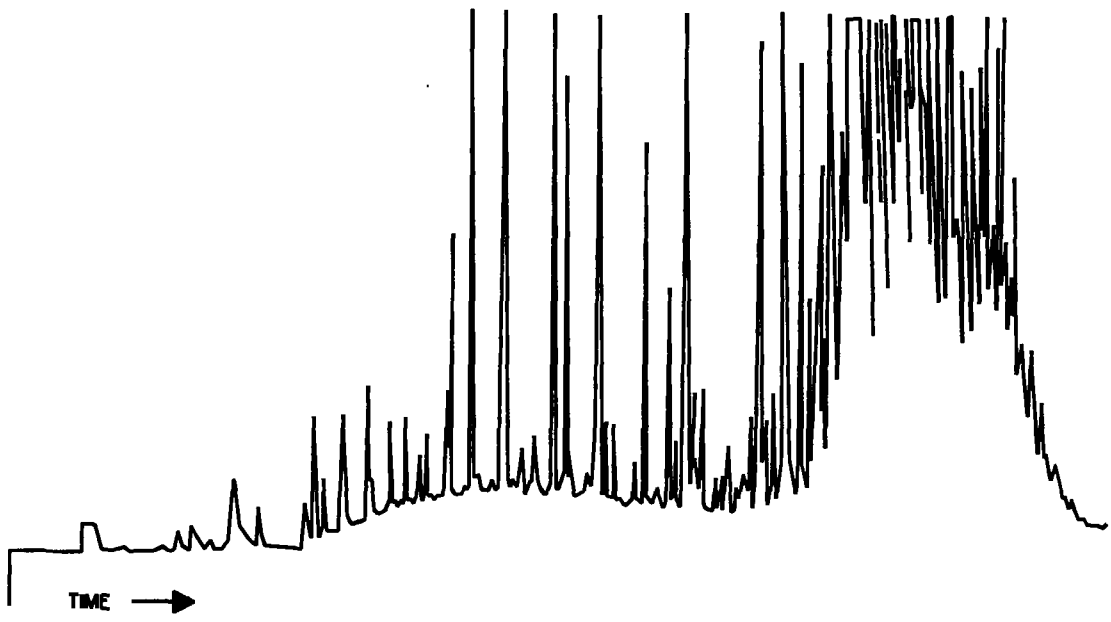


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]



(a). Certified Sampler



(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).

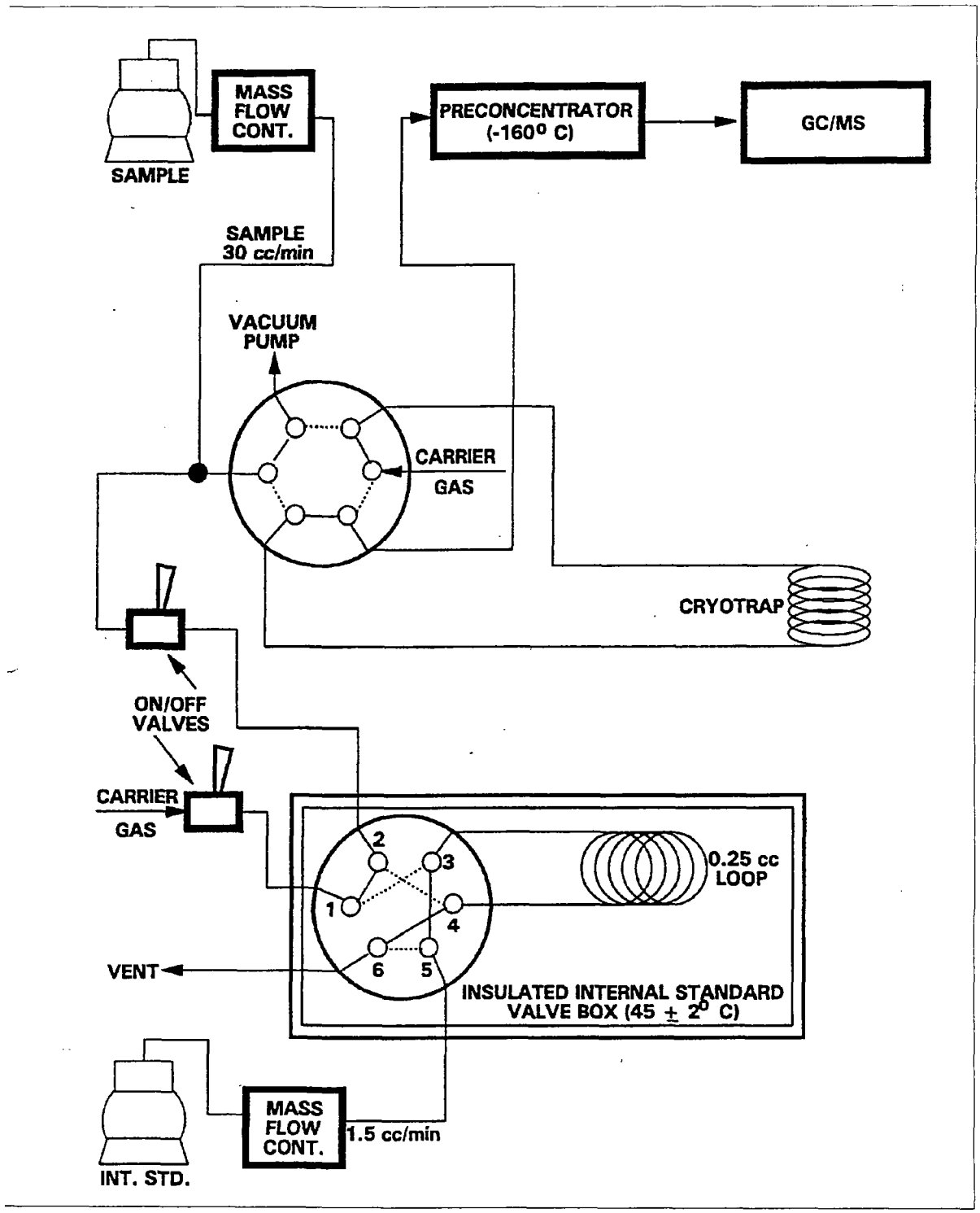


Figure 13. Diagram of design for internal standard addition.

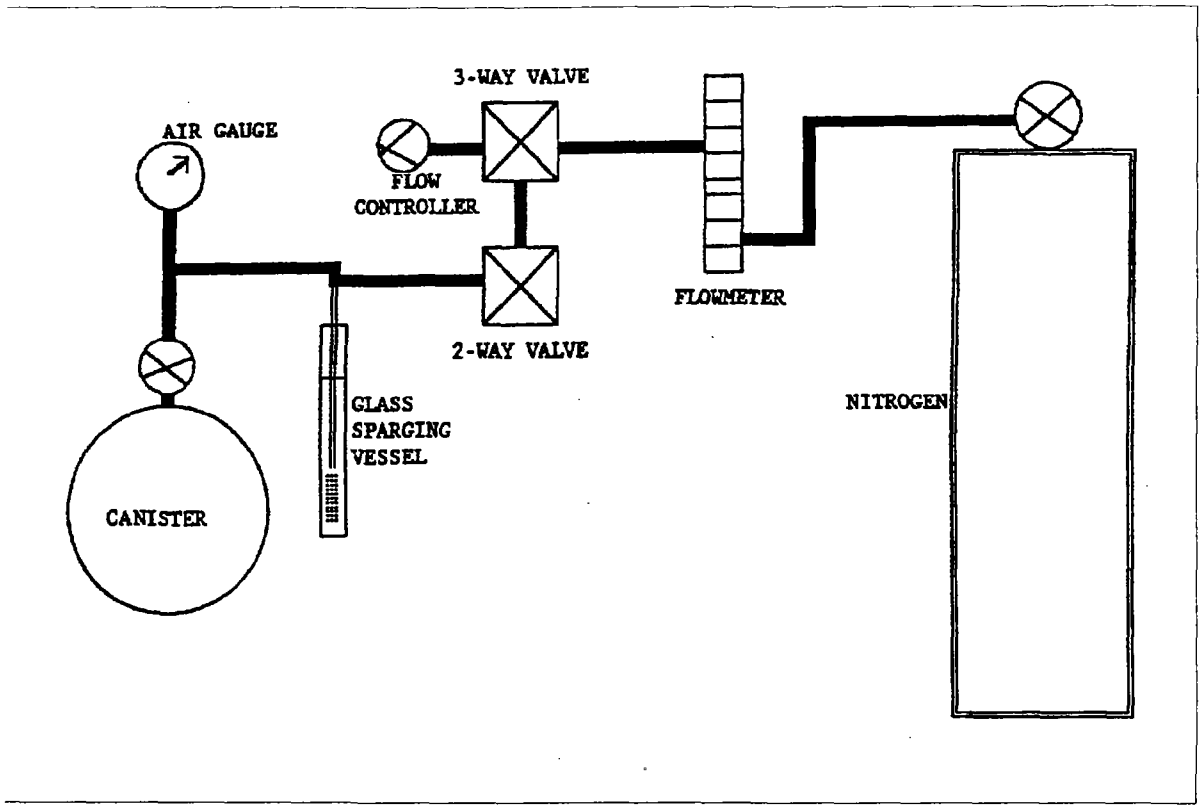


Figure 14. Water method of standard preparation in canisters.

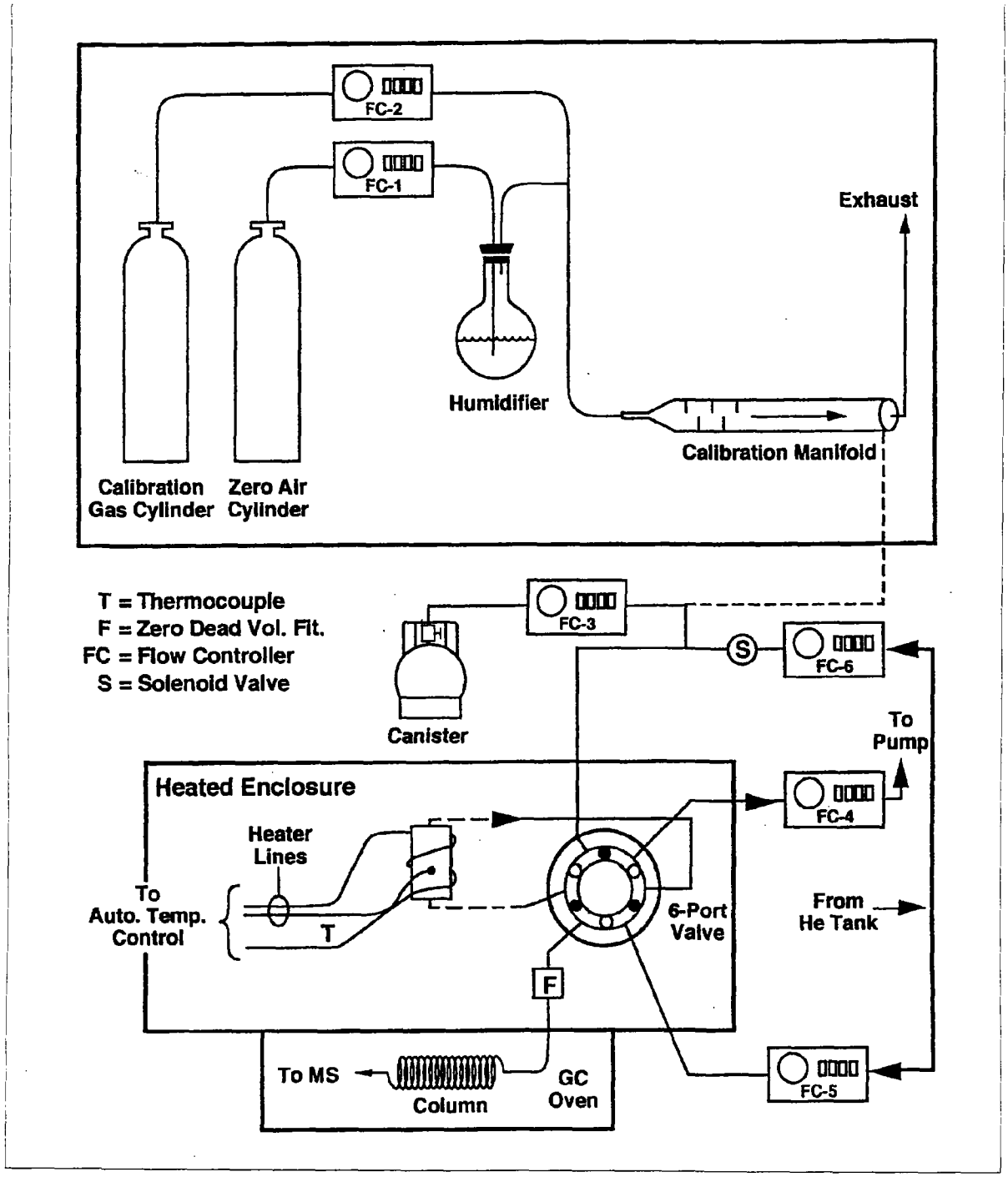


Figure 15. Diagram of the GC/MS analytical system.

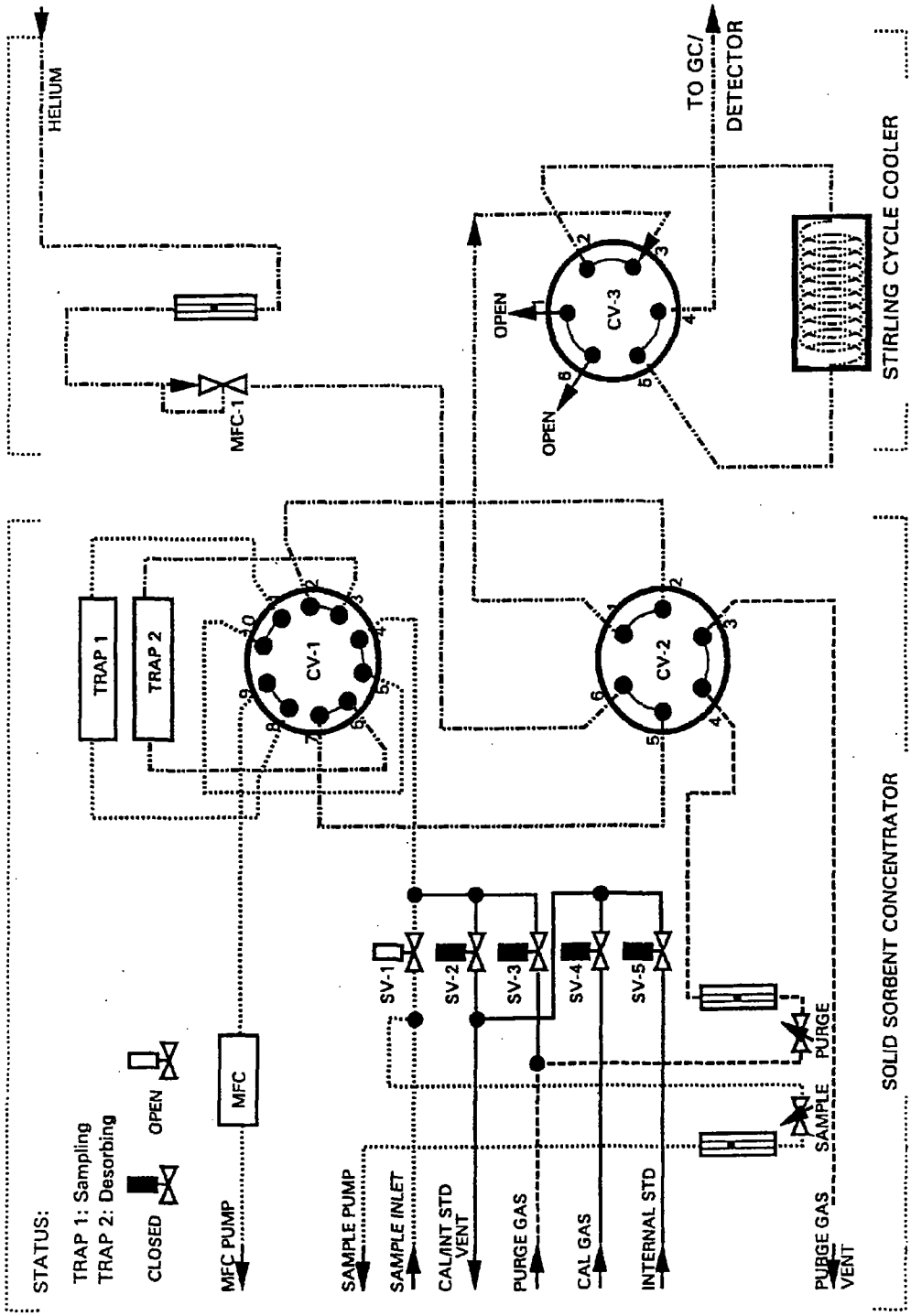


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).